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NEW SUPERCONDUCTORS

STANFORD UNIVERSITY

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13. ABSTRACT This report covers work on the study of possible high temperature superconductors. It describes theoretical work on filamentary organo-metallic materials - the conduction mechanism, band theory, and screening; progress towards the synthesis of metallic chain compounds and related organo-metallic complexes, and experimental studies of their solid state properties.			

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FINAL TECHNICAL REPORT

August 1, 1970 - July 31, 1973

NEW SUPERCONDUCTORS

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I. INTRODUCTION

This is the final report on a program of study aimed at obtaining a better understanding of the problem of preparing materials capable of superconducting at relatively high temperatures via the excitonic interaction. While no new superconducting materials were prepared during the period of the Contract, substantial progress was made in understanding several of the basic theoretical problems and in extending detailed calculations to realizable systems. At the same time a variety of novel materials have been prepared and these have opened the way to some promising routes to a model excitonic system.

There was insufficient time to complete the first phase of the theoretical work but it is estimated that this will be done by the end of 1973. This phase represents a full calculation of the transition temperature of one class of an extremely promising type of compound based on the Krogmann salts. This work is described in the section by D. Davis. Preliminary results indicate that this is a rare situation in which the excitonic coupling could provide a net interaction which would take the system into the strong coupling regime. These results need to be checked thoroughly but provided this conclusion remains it would be well worth while to devote a substantial effort to the synthesis of this type of material. In one phase of the synthetic work the monomer to this assumed stacked complex has been successfully synthesized. This compound provides us with the geometry of the structures needed for the calculations of T_c . The method of preparation of this material is described in the section by C. McAllister.

The work on the band structure of the Pt-complexes outlined in earlier reports has been completed and is being prepared for publication. A paper on this will be given by A. Abarbanel at the A.P.S. meeting in Berkeley in December. Mr. A. Abarbanel obtained his Ph.D. degree for this work. Also a calculation

of the dynamic screening of the Coulomb field in a filamentary compound has been solved exactly within the RPA scheme. This constitutes the Ph.D. thesis of Mr. B. Bush and a full paper on this is in the course of preparation. The details of the calculation of T_c for the filamentary compounds will be presented at the A.P.S. meeting in Berkeley by D. Davis and W. A. Little. A full paper is in the course of preparation. A short communication on the synthetic work of Dr. C. McAllister is also in preparation. The details of the work and an overview of the accomplishments in the preparation of molecular macromolecules with backbones comprised of co-valent intermetallic bonds is contained in the section on Synthesis. Details of the X-ray work on the Rhodium (DOH) system is given and finally, a brief report on transport in Iridium Carbonyl Halides.

II. THEORETICAL SECTION

Numerical Calculations of T_c for Linear Compounds

D. Davis

A. Gap Equation

The approach used to calculate the superconducting transition temperature is that developed by Kirzhnits, Maksimov, and Khomskii.¹ Their method is based on an integral equation for the anomalous pair propagator. This equation is shown diagrammatically in Fig. 1 and given by the equation:

$$F(p, i\omega_n) = -G(p, i\omega_n)G(-p, -i\omega_n)T_c \sum_m \int \frac{d^3k}{(2\pi)^3} V_{\text{eff}}(p-k, i\omega_n - i\omega_m) F(k, i\omega_m). \quad (1)$$



Fig. 1

Using the methods of finite temperature field theory one can show that the spectral weight function for the anomalous propagator, $f(p, x)$:

$$F(p, x) = \int_{-\infty}^{\infty} \frac{f(p, x) dx}{i\omega_n - x}, \quad (2)$$

is given by the integral equation:

$$f(p, x) = - \int \frac{d^3k}{(2\pi)^3} \int_0^{\infty} dy \tanh\left(\frac{y}{2T_c}\right) K(p, k, x, y) f(k, y) \quad (3)$$

where

$$K(p, k, x, y) = V_0(p-k) \left\{ \frac{\delta(x - |\xi_p|)}{2|\xi_p|} \left[1 - \int_0^\infty dE \rho(p-k, E) \left(\frac{1}{E+y+x} + \frac{1}{E+y-x} \right) \right] + \frac{P}{x^2 - \xi_p^2} \rho(p-k, x-y) \theta(x-y) \right\}$$

V_0 is the Coulomb interaction between electrons,

ξ_p is the electron energy measured from the Fermi level,

and $\rho(q, E)$ is the spectral density of the inverse effective dielectric function.

In the model we are considering the presence of an electronically excitable medium modifies the interaction between electrons from the direct Coulomb interaction, $V_0(q)$, to the effective interaction $V_{\text{eff}}(q)$. This is given diagrammatically in Fig. 2,

$$V_{\text{eff}}(q) = V_0(q) + V_0(q) \pi^*(q, \omega) V_{\text{eff}}(q)$$

Fig. 2

where $\pi^*(q, \omega)$ is the proper polarization propagator.²

In terms of the dielectric function the effective interaction is given by:

$$V_{\text{eff}}(q) = \frac{V_0(q)}{1 - \pi^*(q, \omega) V_0(q)} = \frac{V_0(q)}{\epsilon_{\text{eff}}(q, \omega)}, \quad (4)$$

and the spectral density function is given by:

$$\frac{1}{\epsilon_{\text{eff}}(q, \omega)} = 1 - \int_0^\infty \frac{dE^2 \rho(q, E)}{E^2 - \omega^2 - i\delta}. \quad (5)$$

If we define the gap function by

$$\phi(p) = 2|\xi_p| \int_0^{\infty} f(p, x) dx \quad (6)$$

then the integral equation for the gap function is found to be

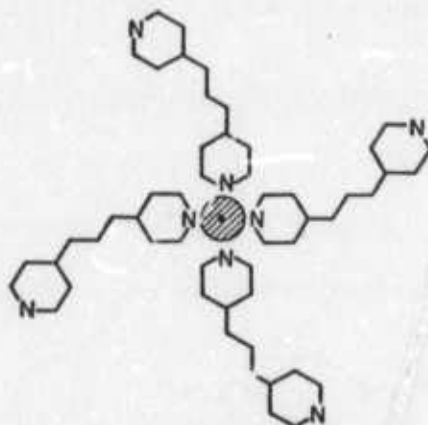
$$\phi(p) = -\int \frac{d^3k}{(2\pi)^3} V_o(p-k) \tanh\left(\frac{|\xi_k|}{2T_c}\right) \frac{\phi(k)}{2|\xi_k|} \left(1 - 2 \int_0^{\infty} \frac{dE \rho(p-k, E)}{E + |\xi_k| + |\xi_p|}\right) \quad (7)$$

where only the term singular at $T_c = 0$ has been retained.¹ The compounds of interest to us have chain like structures. Such chains, if uninterrupted by crystal defects form nearly one-dimensional conducting systems. To describe these we modify the gap equation for a one-dimensional system.

$$\phi(p) = -\int_{-\pi}^{\pi} \frac{dk}{2\pi} V_o(p-k) \tanh\left(\frac{|\xi_k|}{2T_c}\right) \frac{\phi(k)}{2|\xi_k|} \left(1 - 2 \int_0^{\infty} \frac{dE \rho(p-k, E)}{E + |\xi_k| + |\xi_p|}\right) \quad (8)$$

B. Parameters of the One-Dimensional Conducting System

The particular model system of interest is one in which a partially oxidized platinum atom is surrounded by four cyanine dye molecules arranged with square-planar symmetry. The unit cell is shown in Fig. 3.



4-DYE STRUCTURE

Fig. 3

The Coulomb interaction between electrons is computed using a stack of nine unit cells. The Fourier transform for $V_0(r_1, r_2)$ is given by

$$V_0(q) = e^2 \sum_{\substack{\text{unit} \\ \text{cells}, i}}^{N=4} \frac{\exp(-\lambda r_i) \cos(qr_i)}{(r_i + a)} \quad (9)$$

The denominator takes into account Nishimoto and Mayaga's approximation to the Coulomb repulsion term between electrons in π -orbitals.³ The exponential terms account for the screening of the electrons due to the presence of the metal atom chain.⁴

The calculation of the spectral weight function, $\rho(q, E)$ requires the use of the molecular orbitals for the individual dye molecule.⁵ These have been previously calculated.⁶ Using these molecular orbitals one can calculate the transition densities for the excited states. The spectral weight function is obtained from the imaginary part of the polarization propagator, and the Coulomb interaction. For this calculation we use the lowest order approximation $\pi_0(q, \omega)$, which is computed using a stack of nine unit cells. The frequency part of the spectral weight function is a delta function at the exciton energy of that wave vector:

$$\rho(q, E) = \rho(q) \delta(E - E_q) \quad (10)$$

These exciton energies are obtained by transforming from the individual molecular wave functions to the Bloch wave functions for the stack of cells.⁶ Finally, the spectral density is redefined to include the Coulomb pre-factor. The new function $\tilde{\rho}$, is then the spectral density for the first order interaction given in Fig. 4.



$$V_0(q) \pi_0(q, \omega) V_0(q)$$

Fig. 4

As in the case of the Coulomb interaction between electrons on the chain, the Coulomb terms in β include screening due to the presence of the chain of metal atoms. The results are given in Table 1 for the platinum cyanine complex using the following parameters:

unit cell length $c = 3.40\text{\AA}$
 radius of atom in chain $a = 2.80\text{\AA}$
 number of unit cells $N = 9$
 screening factor $\lambda = .14\text{\AA}^{-1}$

q	$V_0(q)/N$	$\rho(q)/N$	$E(q)$	$V_0(q)/N$ (screened)
0	.7492	2.1376	4.0441	.4018
.35	.6797	1.7408	3.8052	.4112
.70	.5289	.9906	3.2479	.3738
1.05	.4014	.4708	2.6803	.3307
1.40	.3372	.2388	2.2727	.2902
1.74	.3019	.1340	1.9954	.2799
2.09	.2645	.0716	1.7810	.2524
2.44	.2368	.0402	1.6339	.2297
2.79	.2326	.0318	1.5708	.2267
3.14	.2361	.0318	1.5592	.2300

Table 1

Parameters for Cyanine Dye Model

An additional term, the screening due to higher excitations of the dye molecules was also calculated.⁶ This screening can modify the Coulomb interaction, as given by Eqn. 4, reducing it by nearly a factor of two. The screened interaction is included in Table 1.

The band of electronic states ξ_k , were calculated by Abarbanel for a chain of metal atoms surrounded by ligands in a square planar symmetry using a multiple scattering technique and found to have a nearly cosine shape with a band width of 3ev.⁷ The Fermi level was taken to lie at $k = \frac{5\pi}{6}$ for these partially oxidized chain compounds.

C. Numerical Calculation

The gap equation in one dimension, Eqn. 8, is solved by iteration. The interval for the integration can be reduced by noting that the gap function, $\phi(k)$, is an even function of k , thereby requiring an integration only over the interval 0 to π . This, together with the results for the parameters of the system, allow one to write the gap equation in the form

$$\phi(k) = -\frac{1}{2\pi} \int_0^\pi dk \tanh\left(\frac{|\xi_k|}{2T_c}\right) \frac{\phi(k)}{2|\xi_k|} \left(V_o(p-k) - \frac{2\tilde{\phi}(p-k)}{E(p-k) + |\xi_p| + |\xi_k|} + V_o(p+k) - \frac{2\tilde{\phi}(p+k)}{E(p-k) + |\xi_p| + |\xi_k|} \right) \quad (11)$$

This equation, which describes the gap function at the transition temperature, requires a special procedure to handle the factor, $\tanh\left(\frac{|\xi_k|}{2T_c}\right) |\xi_k|^{-1}$ in the limit as the electron energy approaches the Fermi level. To avoid this difficulty the equation is rewritten for zero temperature, in which case the function in the denominator is replaced by $\sqrt{\xi_k^2 + \phi^2(k)}$ as in the BCS theory,⁸ while retaining the same function for $V_{eff}(q)$.

This gives the final form for the gap equation

$$\phi(k) = -\frac{1}{2\pi} \int_0^\pi dk \frac{\phi(k)}{2\sqrt{\xi_k^2 + \phi^2(k)}} \left(V_o(p-k) - \frac{2\tilde{\phi}(p-k)}{E(p-k) + |\xi_p| + |\xi_k|} + V_o(p+k) - \frac{2\tilde{\phi}(p+k)}{E(p+k) + |\xi_p| + |\xi_k|} \right) \quad (12)$$

The computation is performed using a grid of points with closely spaced points near the Fermi level. Since the denominator gives a near delta-like contribution at the Fermi level, in this region the analytical value of the integral is computed. The calculated gap function has been found to be independent of the number of grid points from 40 to 300 points, and a grid of 60 points is used. The gap function is also independent of the initial trial solution. The transition temperature is calculated from the maximum value of the gap function using the expression:⁸

$$1.76k_B T_c = \phi_{\max} . \quad (13)$$

At the present time we have finished debugging the computer program and running stability tests. We plan to calculate the transition temperatures for a variety of input parameters to determine which variations contribute to increasing temperatures and to obtain the functional dependencies.

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Stacked Transition Metal Chelate Systems

C. McAllister

September 1973

Introduction

The proposition by Little¹ that a conducting spine of atoms surrounded by a polarizable medium might demonstrate anisotropic excitonic superconductivity has stimulated several new areas of synthetic and preparative chemistry. The Little-Collman approach has been concerned with the synthesis of metal-metal bonded conducting chains, surrounded by various organic dye molecules, to induce and to support the electrical properties of the spine.

Dyestuffs as Ligands for Transition Metals:

Theoretical predictions of the character and structure of the organic polarizable medium immediately suggested various well known dyestuffs, especially those based on the cyanine structure, (Fig. 1).² A critical feature in the design of a suitable transition metal chelate system is the distance between the conduction axis (the metal atoms of our model), and the dye moiety itself. Early attempts toward structurally useful dyestuffs were based on the functionalization of well-known metal ligands, such as glyoximes and acetylacetonates.³ These species were apparently unsuitable mainly because

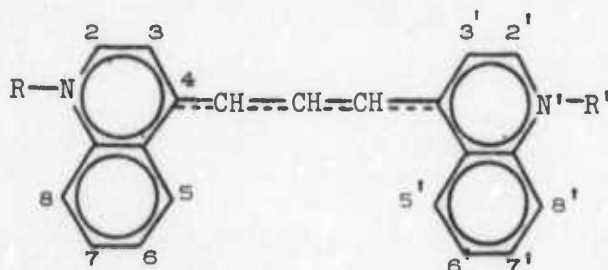


Fig. 1 Generalized Cyanine Dye Structure $R = R' = \text{CH}_2\text{CH}_3$

the ligand group "spaced" the dye moiety too far away from the metal spine. Newer approaches have been to directly attach the dyestuffs to the several transition metals of choice.⁴ As in Figure 1, early attempts coupled the metal atom directly to one of the nitrogen atoms ($R = Ir^{1+}$ or Pt^{2+}). But these models proved unsuitable for other reasons. The 8-hydrogen atom of the quinoline moiety attached to the metal could sterically interfere with other ligands of the metal atom. This interference severely distorted the planarity of the metal chelate system, which reduced the metal-metal interaction between each plane of ligands. Furthermore, no more than one dyestuff could be attached successfully to each metal ion by this general method. That so few dye moieties were associated with each metal atom was another severe limitation of these original model compounds. Work was then initiated to devise systems which avoided these difficulties.

Present Model Studies

Major effort has been concentrated on one general dye-ligand system based on 1,10-phenanthroline, (Fig. 2). The outstanding conceptual feature

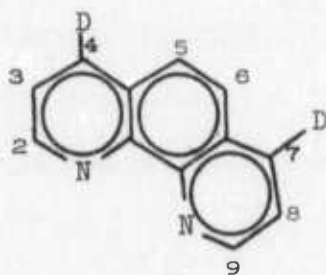


Fig. 2 Dye-ligand system based on 1,10-Phenanthroline
D = derivatized CH_3 group.

of this system is the possibility of coordinating 4 dye moieties, D, directly to a platinum central-spine atom, all in one plane. This arrangement should both minimize steric crowding of extended chains of unsaturated dyes, as well

as maximize dipole-to metal electronic interactions. Layer-to-layer interactions between ligands can be reduced by a rotation about the spine axis.

Two other ligand systems have been proposed which provide for the additional features of ionic charge neutralization or substitution for ligands of known crystal structure, (Fig. 3).

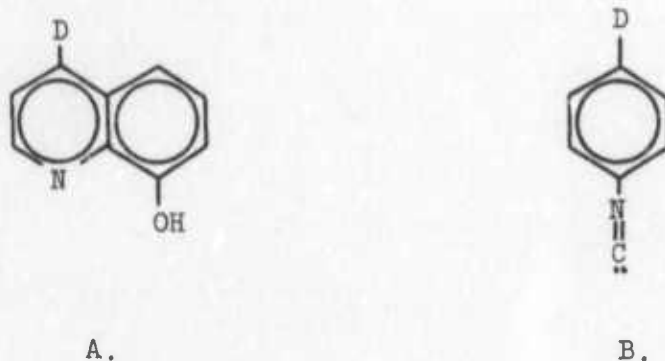


Fig. 3 Dye-ligand systems based on 8-Hydroxy-quinoline A, or p-Toluidine isonitrile B. D = derivatized CH_3 group.

Synthetic Work

The synthesis and initial characterization of dye species V was performed in these laboratories (Fig. 4). This work is summarized below in the Experimental Section. Most noteworthy are the optical measurements on species (V). In acetone/pyridine solution the free dye exhibits an expected sharp absorption maximum at 705nm with another smaller absorption maximum at 650nm. The molar extinction coefficient for the 705 peak is 3.1×10^5 . Upon complexation with Pt^{2+} (by mixing with $(\text{C}_6\text{H}_5\text{CH})_2\text{PtCl}_2$) the spectral characteristics change dramatically. The peak position shifts slightly to 710nm but the

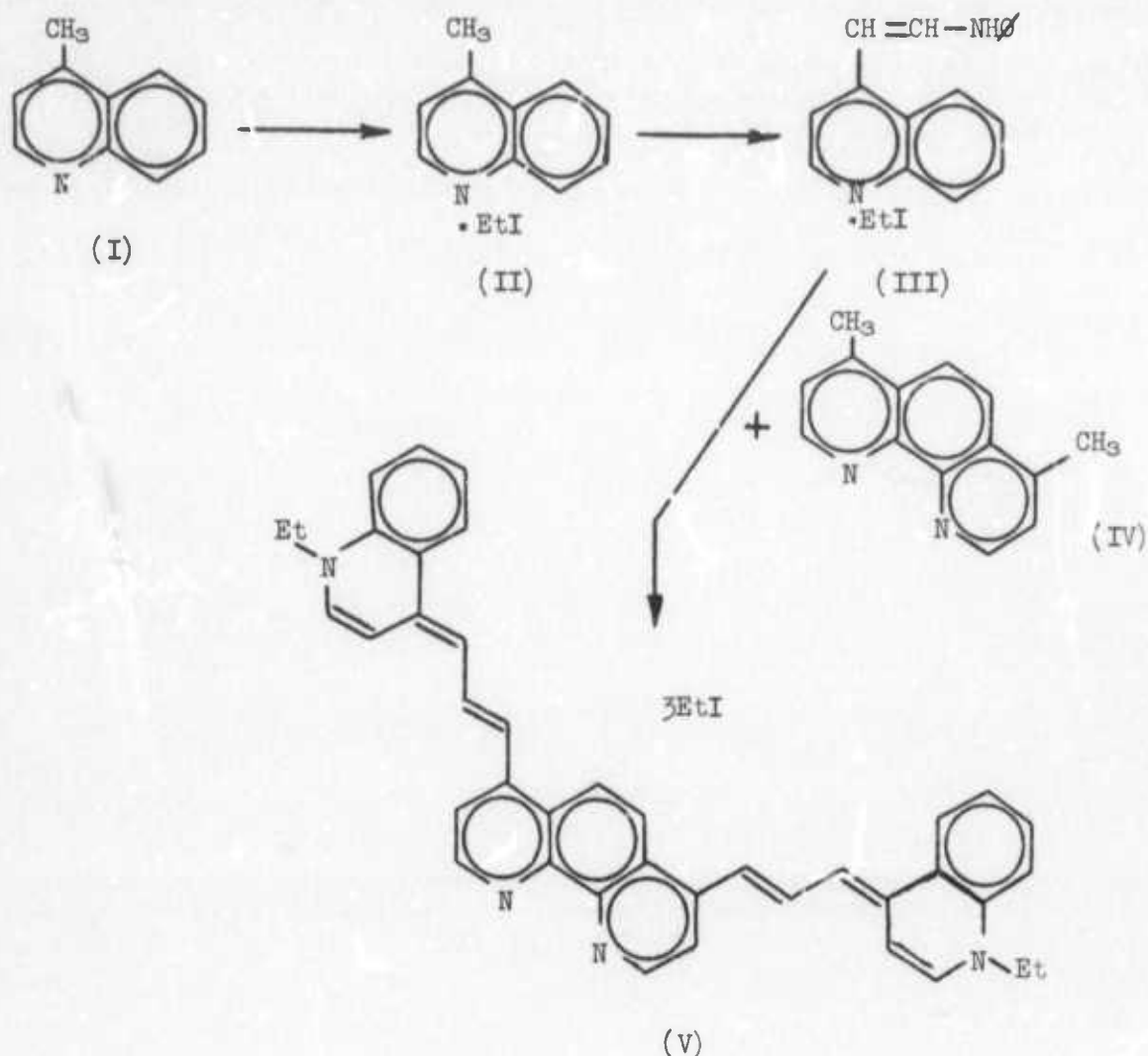


Fig. 4 Synthetic Scheme to A phenanthroline ligand-dye system

extinction coefficient increases to 1.8×10^6 . We interpret this evidence as strongly suggestive of an electronically interactive platinum complex. Isolation and recrystallization of this material from 2:1 chloroform/benzene (dark blue solution) yielded small star-clusters of metallic gold crystals. This material is presently under close examination in these laboratories.

Additionally, the analogous compound with a 2-carbon shorter methine chain in each dye-moiety has been synthesized by a similar route. This compound awaits further characterization.

LEPIDINE ETHIODIDE (II): Crude LEPIDINE (I) (Research Organic/Inorganic or Aldrich #15,828-3) (60.1g, 0.42mol) was mixed with an excess of ethyl iodide (>66g) and ethanol. The mixture was brought to reflux and heated for 7 hours. Upon cooling to 5° a yellow solid formed. Repeated re-crystallizations from ethanol/ether gave 118.1g (94%) yellow prisms.

MP. 141-142.5 Anal: Calc: C 48.17, H 4.71, Found: C 47.95, H 4.75.

PMR. (δ /TMS) 1.94 (3H) trip, 3.10 (3H) sing, 5.19 (2H) quar., 8.0-9.9 (6H) mult.

4-(β -ANILINOVINYL)-QUINOLINE ETHIODIDE (III): A mixture of 30.15g lepidine ethiodide (II) (0.11mol), 20ml ethyl orthoformate, 15ml aniline, and 50ml benzene was heated to reflux for 30 minutes. The mixture was slowly distilled until the distillate had BP \geq 75°. After cooling to 5° and filtration, the solid materials were washed with benzene, and with diethyl ether. Recrystallization from ethanol yielded 39.33g (97%) purple-blue crystals.

MP. 211.5-212.5 Anal: Calc: C 56.71, H 4.72, N 6.96, Found: C 56.24, H 4.78, N 6.96. PMR: 1.8 (3H) trip, 3.1 (1H) broad, 4.7 (2H) quar., 6.8-8.6 (8H) mult.

4,7-[4'-(N'-ETHYLQUINOLINE)-TRIMETHINCYANINE]-1,10-PHENANTHROLINE (V): A solution of 0.214g 4,7-DIMETHYL-1,10-PHENANTHROLINE (J. T. Baker #J-966, or G. F. Smith) (1.03mmol), 4.871g III (12.1mmol), 0.81g KOH (14.5mmol) in 50ml dry ethanol was refluxed for 15 hours. The initially purple solution turned dark green, which became dark blue-green after an additional 10 hours at reflux. Upon cooling and filtration, dark purple crystals with a metallic gold luster were recovered. This solid was washed with benzene, and recrystallized as the tri-ethiodide salt from acetone/benzene.

Yld. 0.42g (72%) MP. 199-200d $\lambda_{\text{max}}^{\text{ACETONE}}$ 705nm, log ϵ 5.21 (shoulder at $\lambda_{\text{max}}^{650}$)

Anal: Calc: C₄₆H₄₉N₄I₃: C 53.19, H 4.75, N 5.39, Found: C 53.47, H 4.70, N 5.65.

PMR: (DMSO' 1.5 (6H) trip, 4.5 (4H) quar., 6.8-8.3 (24H) mult.

BIS-BENZONITRILE PLATINUM (II) CHLORIDE (VI): Using the method of Kharash (J. Am. Chem. Soc. 60:882 (1938)) a portion of PtCl_2 was refluxed in dry benzonitrile for 4 hours. The brown solution was filtered and cooled, to yield pale green needles. The material was found to be 56% benzonitrile + 44% VI.

BIS-{4,7-[4'-(N'-ETHYLQUINOLINE)-TRIMETHINCYANINE]-1,10-PHENANTHROLINE} PLATINUM (II) CHLORIDE: A benzene solution of dyestuff V and benzonitrile-platinum complex VI was prepared in the proportions 3.5:1. Brought to reflux, the mixture was heated for 24 hours to give a dark blue-green suspension with a gold metallic glaze on the walls of the flask. The hot suspension was filtered and the solids washed with dry benzene. The dark blue-green solid was then dried in vacuo @ $65^\circ/0.2\text{mm}$ for 10 hours. As a dark purple, dry solid, the product was taken up in 3:1 acetone/pyridine and chromatographed on alumina. The slowest moving material was mechanically removed and isolated as a dark green-brown solid with a golden luster.

$\lambda_{\text{max}}^{\text{ACETONE}}$ 710nm, log ϵ 6.15, Anal: $(\text{C}_{44}\text{H}_{44}\text{N}_4\text{I}_2)_2\text{PtCl}_2$ FW 1777.6 Calc: C 59.45, H 4.98, Found: C 58.45, H 5.14. A portion was recrystallized from 2:1 chloroform/benzene as golden needles.

Acknowledgement

This author thanks Stanford University Chemistry and Physics Departments for the use of their facilities in this work. In addition, financial support from the Advanced Research Projects Agency is gratefully acknowledged. Fruitful discussions with Professors J. P. Collman and W. A. Little have also been immeasurably valuable in the development of this project.

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III. SYNTHETIC SECTION

This final report on the synthetic section of this project is principally concerned with research accomplished during the past six month period. The earlier reports give an account of previous synthetic projects. During the three years that this grant has been in effect, we have not succeeded in preparing molecular macromolecules whose backbones are comprised of co-valent intermetallic bonds. The reasons for our failure to accomplish this goal within the prescribed period are clear and it is perhaps unreasonable to have expected success in such a brief time frame.

Heavy elements do not use p orbitals in bonding (as carbon does) with the result that most of the reactions modeled after carbon-carbon coupling are unknown in the realm of heavy metal chemistry. The great majority of intermetallic bonds have been formed by metathetical reactions employing anionic, strongly basic metallic reagents. Before we began this work there was considerable evidence that metal-metal bonds could be ruptured by the action of strongly basic reagents. Research performed under the auspices of this contract has provided further examples of this phenomenon.

In the course of this work, we have accomplished several things-- some of which were not among our original synthetic goals. We have synthesized the first examples of transition metal substituted tin hydrides and have developed a general method for preparing the corresponding

transition metal substituted germanium hydrides (a few examples of which were known before the present work). Using these metallo tin and germanium hydrides, we have prepared a series of intermetallic oligomers some of which represent the largest and most diverse co-valent, linear intermetallic compounds yet known. We have provided evidence for coupling reactions with the germanium hydrides which auger well for the eventual synthesis of intermetallic polymers. Even in the absence of continued support, we intend to pursue this avenue at a low level of effort. The synthesis of the neutral square planar rhodium DOH complex is also a notable achievement. This complex represents the most active neutral d^8 compound towards oxidative addition yet reported in the literature. The organometallic chemistry of this compound is fascinating and leaves us with much interesting, unexplored chemistry. Thus far our attempts to add germanium complexes to the rhodium system have been unsuccessful. Nevertheless, the rhodium DOH complex has led us to a series of unusual intermetallic complexes and gives promise for the future development of linear intermetallic polymers. Earlier we established one of the rare cases of cis-trans isomerism among d^6 octahedral compounds with our preparation of the tin-osmium-tin system which was the first linear trimetallic compound. This avenue was abandoned because of the unanticipated isomerism. In the course of this work we also initiated the synthesis of metallic clusters on silica surfaces--a new methodology which may ultimately lead to two dimensional metallic systems.

The following research reports are listed in order. Hoyano describes his work on oligomers containing germanium transition metal bonds. MacLaury discusses some aspects of the fundamental organo-metallic chemistry for the rhodium DOH system--work which was done in order to understand the mechanisms and reactivities of these complexes so that this information could be used to prepare an intermetallic monomer. Stark discusses preliminary experiments intended to introduce trans sulfur or selenium residues into the DOH system. This is a promising approach to linear polymers. Heitner describes the initial attempts to prepare networks of metallic clusters on high porosity silica surfaces. Finally, Fleischer outlines the structural details for the rhodium DOH system. A complete bibliography of published papers carried out under the auspices of this work is collected in this six month report.

It is also appropriate here to indicate experimental difficulties which must be overcome before a project of this type may be successfully pursued. Many of the products we have encountered are insufficiently volatile to be distilled and are quite air-sensitive--especially in solution. Older separation techniques are inadequate to purify these substances so that they may be individually characterized and used in further reactions. Successful pursuit of this research would thus seem to require preparative high pressure liquid chromatography--a technique which is ideally suited to the separation of non-volatile but soluble mixtures of closely related oxygen sensitive substances. The characterization of many of the species

we have encountered is difficult by traditional techniques; although in suitable cases X-ray crystallography can provide the necessary structural information. X-ray photo electron spectroscopy is a technique ideally suited to studying these substances; especially when model compounds are readily available. This is most important in the case of the surface complexes. This new analytical tool was not available to us during the present project. Finally, this work was slowed to some extent by the limited access to inert atmosphere boxes which are necessary for preparative chemistry on such complex materials.

RESEARCH REPORT

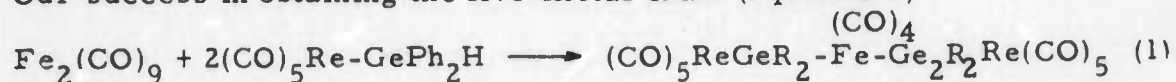
J. K. Hoyano

September 1973

Introduction

Besides suggesting possible routes to covalent intermetallic polymers, our ongoing study of non-ionic metal-metal bond forming reactions coupled with our search for a robust monomer which can be appropriately functionalized and oriented before polymerization has led to the preparation of some novel metal-metal bonded compounds. Related to the coupling reactions employing transition metal germanium hydrides, as discussed in the last report¹, we have found an exceptionally stable Ge-Ge bonded system which remains intact even under fairly basic and ionic conditions. Our investigations so far indicate that a segment of type -Ge-Ge-M- (M=transition metal) may be a good candidate for the backbone of a linear covalent polymer.

Our success in obtaining the five-metal chain (equation 1)

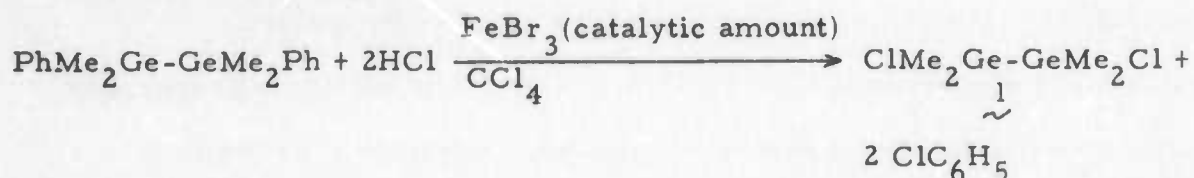


suggested that reaction of $\text{Fe}_2(\text{CO})_9$ or $\text{Na}_2\text{Fe}(\text{CO})_4$ with a difunctional digermane $\text{HR}_2\text{Ge-GeR}_2\text{-H}$ or $\text{Cl-Re}_2\text{Ge-GeRe}_2\text{Cl}$ may have a slight chance of leading to a linear intermetallic oligomer instead of cyclization.

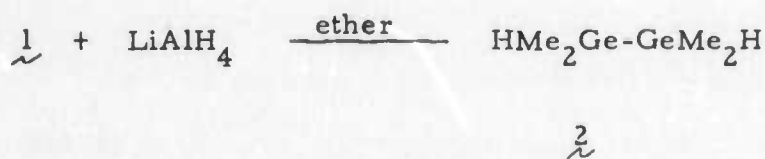
Although numerous transition metal-germanium compounds are now known², only a few of these complexes also contain a Ge-Ge bond and most of the latter are not well characterized. This report outlines the isolation of various compounds possessing the -Ge-Ge-M- moiety.

Results and Discussion

The digermene $\text{ClMe}_2\text{Ge}-\text{GeMe}_2\text{Cl}$ was chosen for investigation because previous work in this laboratory³ had established a high yield synthesis of the diphenyl compound $\text{PhMe}_2\text{Ge}-\text{GeMe}_2\text{Ph}$ and was prepared accordingly. Conversion to the dichloride 1 was achieved readily with dry HCl gas.



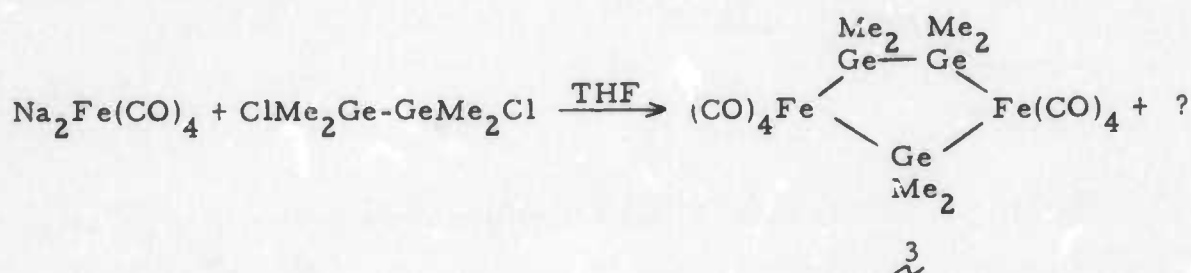
The dichloride 1 is a white low-melting crystalline solid which decomposes readily in air. Conversion of 1 to the dihydride 2 was effected with lithium aluminum hydride in ether solution.



A difunctional digermene such as $\text{HR}_2\text{Ge}-\overset{\text{Rh}}{\underset{\text{DO}}{\text{Rh}}}-\text{GeR}_2\text{H}$ ($\text{Rh}=\text{Rh}(\text{DO})(\text{DOH})_{\text{pn}}$) with its rigid linear 3-metal backbone appeared more desirable than 1 or 2 for attempting an intermetallic polymer. However, at present, methods for bonding germanium to the rhodium system are not available⁴. Consequently both 1 and 2 were reacted with $\text{Na}_2\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ respectively in a one to one molar ratio using various conditions of temperature (-80° to $+35^\circ$) and reaction time (15 minutes to 40 hours).

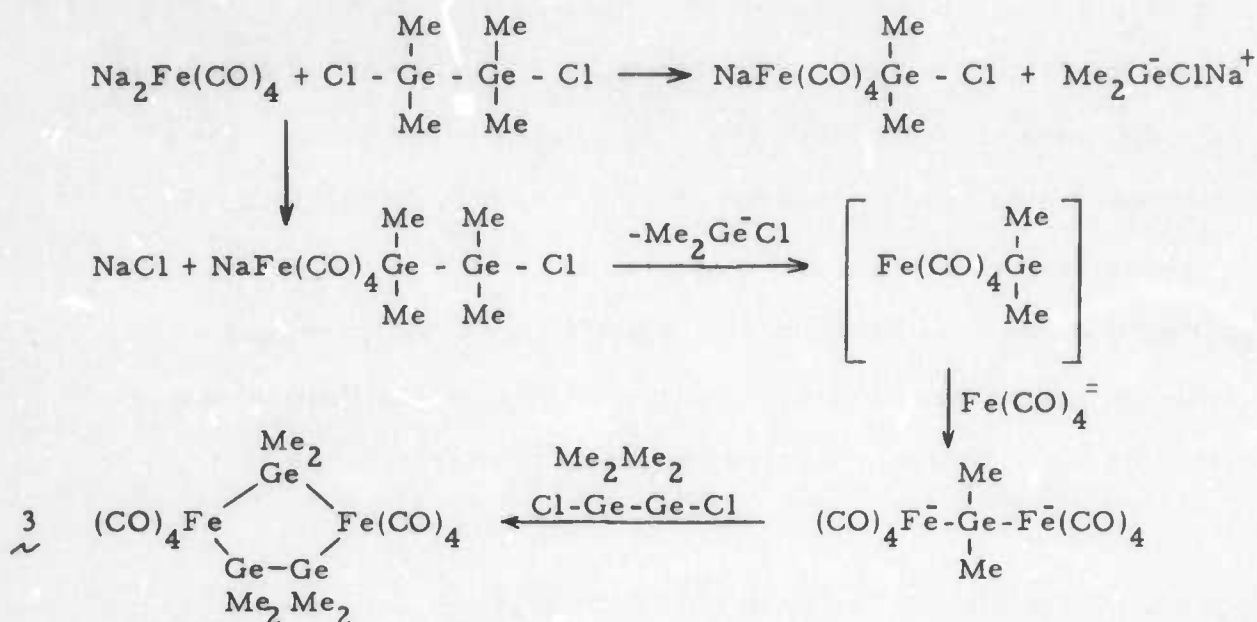
Infrared monitoring in the carbonyl stretching region indicated both 1 and 2 gave the same products with 1 affording slightly better yields. Thus isolation attempts were carried out on reactions with the dichloride.

Using various physical and spectroscopic methods, it became apparent that two main products were being formed. Only the less volatile component was isolated pure by fractional crystallization as a crystalline white solid and has now been fully characterized as 3.

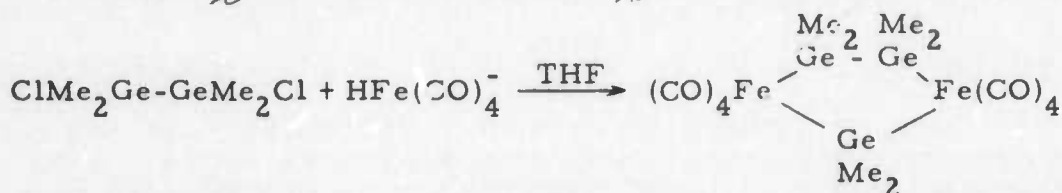


The nmr, ir, mass spectra and elemental analyses are consistent with the structure 3; an X-ray structure determination is in progress. Using column chromatography, fractional crystallization and even preparative TLC, purification of the more volatile product could not be achieved. The ir and nmr spectra of mixtures indicated that this component was very similar to 3.

The mechanism for the formation of 3 is not clear but a possible scheme is shown.

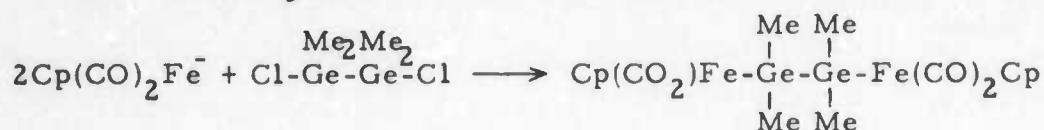


The complex 3 was also obtained when 1 was reacted with $\text{HFe}(\text{CO})_4^-$.



In the above two reactions it appeared that a Ge-Ge bond was cleaved during the course of the reactions. Reaction with simpler monoanionic transition metal ions seemed a logical area for investigation.

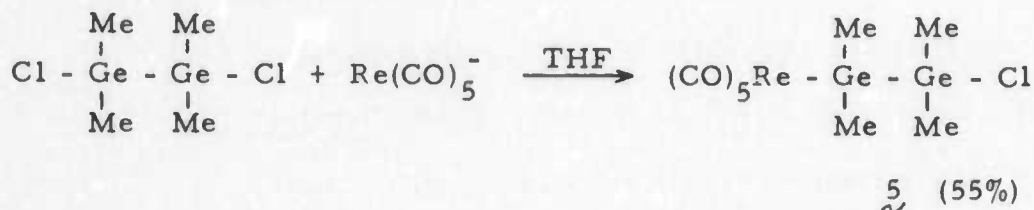
With two moles of the very nucleophilic anion $\text{Cp}(\text{CO})_2\text{Fe}^-$ the 4-metal complex 4 was obtained in good yield as very stable yellow crystals.



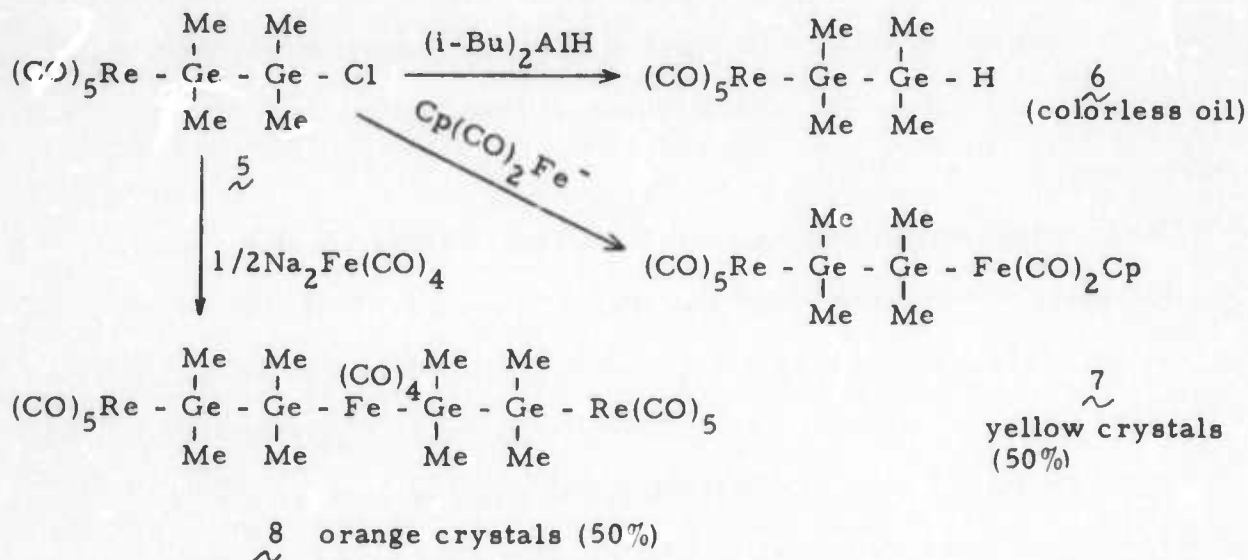
4 (60%)

No evidence was obtained which indicated that cleavage of the Ge-Ge bond had occurred even to a small extent. Previous attempts to cap the hexagermane $\text{I}-[\text{Me}_2\text{Ge}]_6-\text{I}$ with $\text{Cp}(\text{CO})_2\text{Fe}^-$ resulted in cleavage of the germanium chain³. The Ge-Ge bond in shorter chains appears less susceptible to nucleophilic attack.

Reaction of 1 with one mole of $\text{Re}(\text{CO})_5^-$ gave displacement of only one chloride; the product 5 was isolated as white crystals after careful chromatography and sublimation.



Complex 5 underwent further reactions to form longer chain metal oligomers, and is shown in the scheme below.



The formation of 7 in high yield indicates that both the Re-Ge and Ge-Ge bonds are not attacked to any detectable degree by $\text{Cp}(\text{CO})_2\text{Fe}^-$. Also the formation of 8 suggests that the Re-Ge bond may somehow enhance the Ge-Ge bond if one considers the products obtained when the bare dichloride 1 is reacted with $\text{Na}_2\text{Fe}(\text{CO})_4$.

The foregoing discussion gives an indication of the types of transition metal moieties that can be bonded to the Ge-Ge unit and further studies may lead to a suitable monomer for forming a linear covalent intermetallic polymer. It appears that such a monomer must have both a germanium and the transition metal suitably functionalized (with X and Y) before polymerization is attempted. For example:
X-M-Ge-Ge-Y.

Spectroscopic Properties and Structure

Besides elemental analyses, the characterization of the complexes discussed above relied heavily on infrared, nuclear magnetic resonance and mass spectral data. The main features of these properties will now be discussed.

The carbonyl stretching region of the infrared spectrum is a valuable aid in the study of transition metal carbonyl complexes. Both the number and position of the carbonyl bands help in structure determination. Derivatives of rhenium pentacarbonyl ($\text{X-Re}(\text{CO})_5$ - ca. C_{4v} symmetry) have been well studied⁵ and are characterized by three infrared active carbonyl frequencies with a weak to medium band near 2100 cm^{-1} and a strong and very strong band near 2000 cm^{-1} . Depending on the substituent X the positions of the bands may shift as much as 50 cm^{-1} but the relative

pattern remains the same. This consistent pattern is seen in the ir spectra of the rhenium pentacarbonyl derivatives prepared here (see Experimental for frequencies).

In the complex $(\text{CO})_5\text{Re}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\text{Fe}(\text{CO})_2\text{Cp}$, 7, the rhenium and iron are separated by two germanium atoms so little or no vibrational coupling is expected between the carbonyls on the rhenium with those on the iron. The actual spectrum shows bands at 2104 mw and 1997 vs which can be assigned to $\text{Re}(\text{CO})_5$ and the 1992 s and 1946 s bands to the carbonyls on iron. The above argument also holds for the complex

$(\text{CO})_5\text{Re}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\text{Fe}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\text{Re}(\text{CO})_5$, 8, where the four bands

assigned to the $\text{Fe}(\text{CO})_4$ group indicate that the germaniums are bonded in a cis fashion to the iron.

The proton nmr spectra were especially helpful for characterization because of the methyl substituents on the germaniums. Resolvable chemical shift differences were obtained for the unsymmetrical digermanes as seen in the Table below. (Experimental contains more details).

Mass spectra of compounds containing polyisotopic elements such as germanium and most transition metals are invaluable for structure determination if they can be obtained properly at relatively low

temperatures. The mass spectra of $(\text{CO})_5\text{Re}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\text{Cl}$ and $\text{Fe}_2(\text{CO})_8(\text{GeMe}_2)_3$

were obtained in this study and their cracking patterns are informative.

Both complexes display the molecular ion as the highest ion observed.

They also show peaks corresponding to the successive loss of the

appropriate number of carbonyls. i. e., $[(\text{CO})_n\text{Re-Me}_2\text{Ge-GeMe}_2\text{-Cl}]^+$ ($n=0, 1, 2 \dots 5$) and $[\text{Fe}_2(\text{CO})_n(\text{GeMe}_2)_3]^+$ ($n=0, 1, 2 \dots 8$).

TABLE--NMR Data for Tetramethyldigermene Derivatives

<u>Compound</u>	<u>tau for Ge-CH₃</u>	<u>resonances</u>
$\text{PhMe}_2\text{Ge-GeMe}_2\text{Ph}$	9.55	singlet
$\text{ClMe}_2\text{Ge-GeMe}_2\text{Cl}$	9.10	singlet
$\text{Cp}(\text{CO})_2\text{Fe-Me}_2\text{Ge-GeMe}_2\text{-Fe}(\text{CO})_2\text{Cp}$	9.23	singlet
$(\text{CO})_5\text{Re-Me}_2\text{Ge-GeMe}_2\text{-Cl}$	9.26	singlet 9.23 singlet
$(\text{CO})_5\text{Re-Me}_2\text{Ge-GeMe}_2\text{-H}$	9.62	doublet 9.25 singlet
$(\text{CO})_5\text{Re-Me}_2\text{Ge-GeMe}_2\text{-Fe}(\text{CO})_2\text{Cp}$	9.40	singlet 9.23 singlet
$[(\text{CO})_5\text{Re-Me}_2\text{Ge-GeMe}_2]_2\text{Fe}(\text{CO})_4$	9.25	singlet 9.17 singlet

Experimental

A dry argon atmosphere was maintained during all reactions and during work-up by using Schlenk apparatus. All solvents and reagents were dried or purified when necessary by standard procedures.

Infrared spectra were recorded on a Perkin-Elmer model 421 grating spectrometer using hexane as solvent in 1 mm path length KBr cells.

Nuclear magnetic resonance spectra were obtained with a Varian T-60 instrument. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalyses were performed by the Stanford Microanalytical Laboratories.

1,2-Dichlorotetramethyldigermene, $\text{Cl}-\text{Ge}^{\text{Me}_2}-\text{Ge}^{\text{Me}_2}-\text{Cl}$

The dimer $\text{PhGe}^{\text{Me}_2}-\text{Ge}^{\text{Me}_2}\text{Ph}$ was prepared by the sequence of reactions reported by M. Cooke and R. Stark in earlier technical reports³. A typical preparation of the dichloride follows.

A solution of $\text{PhGe}^{\text{Me}_2}-\text{Ge}^{\text{Me}_2}\text{Ph}$ (10 g, 28 mmol) in 30 ml of CCl_4 containing 50 mg of FeBr_3 was treated with dry HCl gas (moderate rate of bubbling) for 30 minutes and then the HCl saturated mixture was stirred for three hours. The reaction progress was monitored by nmr spectroscopy. The above bubble and stir cycle was repeated two more times after which the nmr spectrum indicated complete reaction. Fractional distillation of the mixture yielded a colorless oil which formed white crystals (6.0 g, 81%) of the product on standing: mp 43-46°; bp 92-95°/20 mm; nmr (CCl_4) τ 9.10 (singlet).

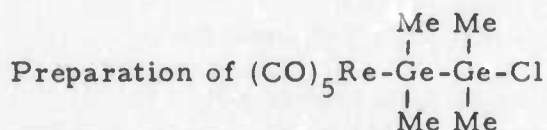
1,2-Bis(cyclopentadienyldicarbonyliron)tetramethyldigermene,

$\text{Cp}(\text{CO})_2\text{Fe}-\text{GeMe}_2-\text{GeMe}_2-\text{Fe}(\text{CO})_2\text{Cp}$

A solution of $\text{Cl}-\text{GeMe}_2-\text{GeMe}_2-\text{Cl}$ (275 mg, 1.0 mmol) in 4 ml of THF was treated with $\text{NaFe}(\text{CO})_2\text{Cp}^6$ (1 mmol in 15 ml THF) and the resulting mixture was stirred for 17 hours at room temperature. Evaporation of the THF at reduced pressure followed by extraction with 20 ml of benzene and then evaporation to dryness yielded 0.53 g of crude product (yellow-brown solid). Crystallization from hexane-toluene afforded 0.34 g (60%) of yellow crystals: mp 143-147° (with decomposition); nmr (C_6D_6) τ 9.23 (singlet, 6H, $\text{Ge}-\text{CH}_3$) and 5.75

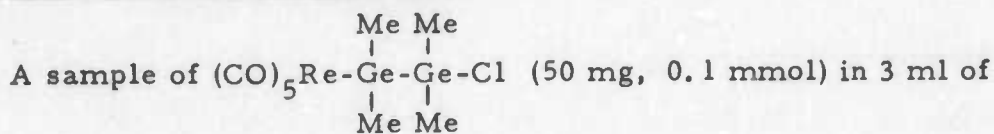
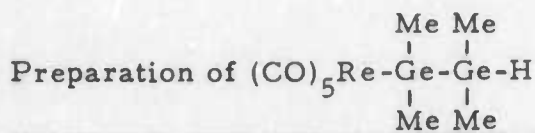
(singlet, 5H, cyclopentadienyl protons); ir (hexane) 1996s, 1988vs, 1944vs and 1936s sh cm^{-1} ; molecular weight--found (CHCl_3) 560, calcd 559.

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Fe}_2\text{Ge}_2$: C, 38.66; H, 3.97; Fe, 19.96; Ge, 25.96. Found: C, 38.69; H, 3.99; Fe, 19.5; Ge, 24.96.

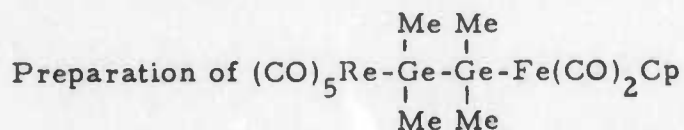


A $\text{NaRe}(\text{CO})_5$ solution (prepared by stirring 1.89 g (2.90 mmol) $\text{Re}_2(\text{CO})_{10}$ in 20 ml of THF for 30 minutes with excess sodium amalgam) was added to $\text{ClMe}_2\text{Ge}-\text{GeMe}_2\text{Cl}$ (1.60 g, 5.80 mmol) in 5 ml of THF. The reaction mixture was stirred for 21 hours before evaporating to dryness at reduced pressure. Extraction of the residue with 20 ml of benzene and evaporation gave a yellow oil. This oil was chromatographed on silica gel (35 g). Elution with hexane gave a small amount of $\text{Re}_2(\text{CO})_{10}$; chloroform elution afforded crude product as a colorless oil which was sublimed slowly (30°) onto a 10° probe to yield white crystals (1.80 g, 55%) of the product: mp $40-42^\circ$; nmr (CCl_4) τ 9.26 singlet, 6H) and 9.23 (singlet, 6H); ir (hexane) 2115m, 2042w, 2003vs and 1997 cm^{-1} ; molecular weight (mass spectroscopically), highest observed ion corresponds in mass units and pattern to that calculated for the molecular ion.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_5\text{ClReGe}_2$: C, 19.06; H, 2.13; Cl, 6.25. Found: C, 18.87; H, 2.10; Cl, 6.13.

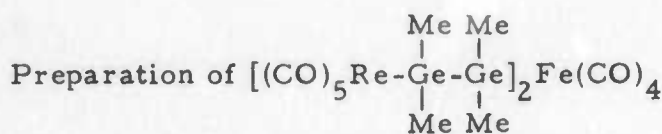


hexane was treated with $(i\text{-Bu})_2\text{AlH}$ (0.3 ml of a 1.0 M heptane solution); the solution was stirred for 19 hours. The whole reaction solution was filtered through a short silica gel column with 30 ml of benzene. Evaporation of the filtrate yielded 30 mg of product as a colorless oil: nmr (C_6D_6) τ 9.62 (doublet, 6H), 9.25 (singlet, 6H) and 5.80 (septet, 1H); ir (hexane) 2109m, 2000vs and 1995s cm^{-1} .



A solution of $(\text{CO})_5\text{Re}-\begin{array}{c} \text{Me Me} \\ | \quad | \\ \text{Ge-Ge-Cl} \\ | \quad | \\ \text{Me Me} \end{array}$ (100 mg, 0.18 mmol) in 4 ml of THF was treated with a 1 ml THF solution containing 1 equivalent of $\text{NaFe}(\text{CO})_2\text{Cp}$. Magnetic stirring for 2 hours, evaporation to dryness, extraction with 10 ml of benzene and finally evaporation at reduced pressure gave a crude solid yellow-brown product. Crystallization from hexane afforded yellow plates (60 mg, 48%) of the product: nmr (CCl_4) τ 9.40 (singlet, 6H), 9.23 (singlet, 6H) and 5.27 (singlet, 5H); ir (hexane) 2104mw, 1997vs, 1992ms and 1946m cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{FeGe}_2\text{Re}$: C, 27.13; H, 2.42; Fe, 7.88.
Found: C, 27.18; H, 2.50; Fe, 8.06.



A mixture of $(\text{CO})_5\text{Re}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Ge}}}-\text{Cl}$ (100 mg, 0.18 mmol) and $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$ dioxane (32 mg, 0.09 mmol) was stirred in 5 ml of THF for 17 hours before evaporating to dryness at reduced pressure. The solid residue was crystallized from 10 ml of hexane to afford 60 mg (50%) of yellow needles: nmr (CDCl_3) τ 9.25 (singlet, 6H) and 9.17 9.17 (singlet, 6H); ir (hexane) 2107m, 2051m, 2002vs, 1994s, 1985ms, 1973m and 1955msh cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_{14}\text{FeGe}_4\text{Re}_2$: C, 21.47; H, 1.97; Fe, 4.54. Found: C, 21.73; H, 2.07; Fe, 4.36.

Preparation of $\text{Fe}_2(\text{CO})_8(\text{GeMe}_2)_3$

A mixture of $\text{ClMe}_2\text{Ge}-\text{GeMe}_2\text{Cl}$ (200 mg, 0.72 mmol) and $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1-1/2$ dioxane (240 ml, 0.70 mmol) was stirred in 5 ml of THF at -78° for two hours before allowing to warm slowly to room temperature. Stirring was continued for an additional 10 hours before evaporation to dryness. The residue was fractionally crystallized three times from hexane to afford white crystals of the product (110 mg, 25%): mp decomposes above 160° ; nmr (C_6D_6) τ 9.23 (singlet, 12H) and 8.75 (singlet, 6H); ir (hexane) 2069w, 2049s, 1998vs and 1990ms cm^{-1} ; molecular weight, found 644 (CHCl_3), calculated is

643.75; mass spectrometrically the highest observable fragment corresponds in mass and pattern to that calculated for the molecular ion.

Anal. Calcd for $C_{14}H_{18}O_8Fe_2Ge_3$: C, 26.13; H, 2.82; Fe, 17.35.
Found: C, 26.05; H, 2.79; Fe, 17.8.

References

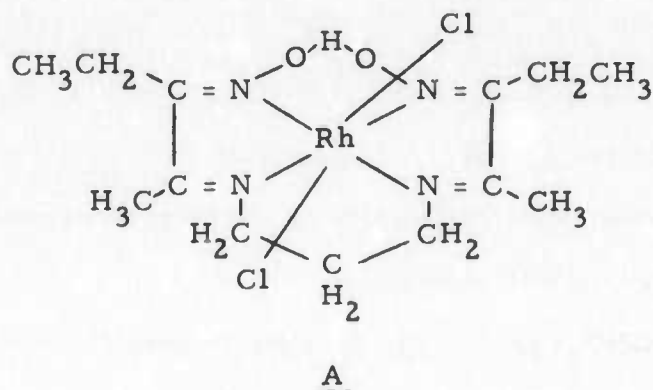
- (1) J. Hoyano, Fifth Semi-Annual Technical Report, January, 1973.
- (2) Reference 1, reference number 4b.
- (3) M. Cooke and R. Stark, First Semi-Annual Technical Report, January, 1971.
- (4) R. Stark, Sixth Semi-Annual Technical Report, September, 1973.
- (5) F. A. Cotton and C. S. Kraihanzel, J. Amer. Chem. Soc., 84, 4432 (1962); J. B. Wilford and F. G. A. Stone, Inorg. Chem., 4, 389 (1965); W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. G. Graham, Inorg. Chem., 5, 2217 (1966) and references therein.
- (6) R. D. Gorsich, J. Amer. Chem. Soc., 84, 2486 (1962); T. S. Piper, O. Lemal and G. Wilkinson, Naturwissenschaften, 43, 129 (1956).

RESEARCH REPORT

Michael R. MacLaury

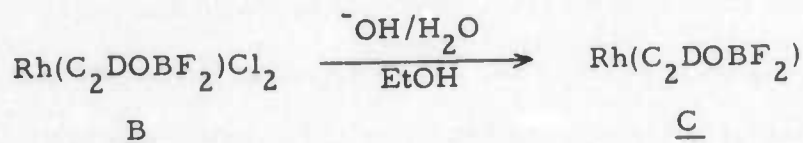
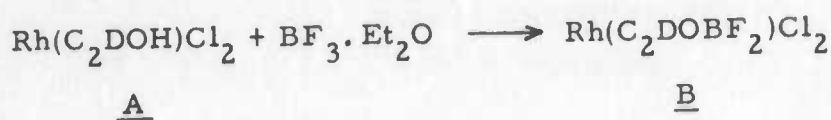
September 1973

Work on the rhodium(I) system first reported by Collman, Murphy, and Dolcetti¹ has continued. Because the [3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato]rhodium(I), Rh(DO)(DOH), is very insoluble in solvents such as THF and dimethoxyethane, the ligand was modified to give a more soluble compound. 3-Oximino-2-pentanone² was treated with 1,3-propane diamine to yield the [3,3'-(trimethylene dinitrilo)-di-2-pentanone dioximato](-1) ligand (C₂DOH). Rhodium was inserted into the ligand¹ to give A.



Compound A, Rh(C₂DOH)Cl₂, was treated with BF₃·Et₂O to give B, Rh(C₂DOBF₂)Cl₂, where the hydrogen of the oxime bridge has been replaced with BF₂. This material can be reduced by basic aqueous ethanol

to yield the desired reactive species C, $\text{Rh}(\text{C}_2\text{DOBF}_2)$.



$\text{Rh}(\text{C}_2\text{DOBF}_2)$ is as reactive as $\text{Rh}(\text{DO})(\text{DOBF}_2)$ but is more soluble thus making it easier to measure nmr spectra, purify products, and measure kinetic rates of reactions.

The mechanism of oxidative addition is currently of interest^{3,4,5,6}. The mechanism of alkyl halide addition to transition metals has been reported as proceeding with inversion⁴ in all cases but one where it was reported to proceed with retention⁵. It has also been described as a free radical process⁶. The $\text{Rh}(\text{C}_2\text{DOBF}_2)$ system is well suited to study the chemistry of oxidative addition. The addition products are air stable crystalline compounds that can easily be characterized, and the reaction proceeds under reasonable conditions⁷.

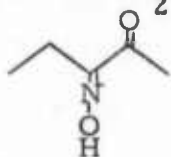
The $\text{Rh}(\text{C}_2\text{DOBF}_2)$ gave trans addition products of a variety of alkyl halides. The adducts of the following halides have been characterized: CH_3I , $\text{CH}_3\text{CH}_2\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $\text{H}_3\text{C}-\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$, n-propylbromide, isopropyl bromide, isopropyl iodide, n-butylbromide, sec-butyl bromide, cis and trans 1,4-dibromocyclohexanes, cis and trans 1-bromo-4-methyl cyclohexanes, 5-bromopentene-1, 6-bromohexene-1, and trans

β -bromostyrene. C also reacts with dry HCl to give $\text{H-Rh}(\text{C}_2\text{DOBF}_2)\text{Cl}$. This material shows a hydride stretching band in the infra-red of the solid but the solution ir (DME) indicates that the hydrido species is in equilibrium with the rhodium(I) species, as no $\nu_{\text{Rh-H}}$ is observed.

Experimental

All reactions that involved the rhodium(I) complex were carried out under nitrogen either in Schlenk apparatus or in an inert atmosphere box. THF and dimethoxyethane, DMF, were distilled from CaH_2 under N_2 in an apparatus that constantly recycled the distillate. These solvents were further deoxygenated once inside the inert atmosphere box by bubbling the box atmosphere through the solvent for a minimum of 20 minutes. The estimated concentration of oxygen in the DME is 2 ppm (0.06 mM). The alkyl halides were purified in all cases by passage through activated basic alumina immediately before use. Microanalyses were performed by the microanalytical laboratory of this department. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrometer. Nuclear magnetic resonance spectra were obtained with either a Varian T-60 or an XL-100 instrument.

3-oximino-2-pentanone,



Methyl nitrite was bubbled into a stirred mixture of 2-pentanone (102g, 1.19 mol), 400 ml diethyl ether, and 15 ml conc. HCl at a rate

to maintain a vigorous reflux. The methyl nitrite was generated by dropping a solution of H_2SO_4 (100 ml) and H_2O (95 ml) onto a stirred slurry of NaNO_2 (112 g, 1.62 mol), methanol (66 g, 2.08 mol) and H_2O (75 ml). After addition of methyl nitrite was complete the ether solution was neutralized with sat. NaHCO_3 . The aqueous layer was washed once with ether. The ether portions were combined and dried over MgSO_4 . The product was crystallized from the ether solution to yield 84.5g (62%).

[3,3'-(trimethylenedinitrilo)-di-2-pentanone dioximate], C_2DOH

The ketoxime (30 g, 0.26 mol) 1,3-propanediamine (9.6 g, 0.13 mol), and 200 ml isopropyl ether were heated under reflux for 3 hours. The product crystallized very slowly (days) from the refrigerated solution to yield 31 g (90%).

Trans-dichloro[3,3'-(trimethylenedinitrilo)-di-2-pentanone dioximate]-rhodium, $\text{Rh}(\text{C}_2\text{DOH})\text{Cl}_2$.

Carbon monoxide was vigorously bubbled through 300 ml ethanol and LiCl (3.4 g). $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ (3.0 g, 40.2% Rh, 11.7 mM) was added to the warmed (70-80°) solution. Five minutes later the ligand, C_2DOH (5.4 g, 20.2 mM) was added. The mixture was heated under reflux and the CO bubbling continued for 2 hours. The yellow flocculent precipitate was collected with the aid of celite filter aid and it was washed with ether. The product was dissolved off the celite with CH_2Cl_2 and crystals formed upon the addition of ethanol to yield 2.44 g (47%). Proton nmr (100 MHz) in CDCl_3 ; δ 1.28 (t, $J=8\text{Hz}$, 6H), δ 2.50 (s, 6H), δ 2.95 (q on M, $J=8\text{ Hz}$, 6H) δ 4.14 (M, 4H).

Anal. Calcd for $\text{RhO}_2\text{N}_4\text{Cl}_2\text{C}_{13}\text{H}_{23}$: C, 35.39; H, 5.25; N, 12.70.

Found: C, 35.00; H, 5.10; N, 12.87.

Trans-dichloro[difluoro[3,3'-(trimethylenedinitrilo)-di-2-pentanone dioximate]borate]rhodium, $\text{Rh}(\text{C}_2\text{DOBF}_2)\text{Cl}_2$.

The $\text{Rh}(\text{C}_2\text{DOH})\text{Cl}_2$ (4.5 g, 10.2 mM) suspended in diethyl ether (50 ml) was treated with boron trifluoride etherate (15 ml). The mixture was stirred overnight to give a yellow powder, which was filtered and washed with ether. The product was recrystallized from CH_2Cl_2 to yield 3.0 g (61%). nmr (100 MHz in CDCl_3); δ 1.26 (t, $J=8$ Hz, 6H), δ 2.58 (s, 6H), δ 2.98 (q on M, $J=8$ Hz, 6H), δ 4.14 (M, 4H).

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{Cl}_2\text{N}_4\text{C}_{13}\text{H}_{22}$: C, 31.93; H, 4.54; N, 11.46.

Found: C, 31.39; H, 4.50; N, 11.48.

[difluoro[3,3'-trimethylene dinitrilo]di-2-pentanone dioximato borate] rhodium I. $\text{Rh}(\text{C}_2\text{DOBF}_2)$.

The $\text{Rh}(\text{C}_2\text{DOBF}_2)\text{Cl}_2$ (1.0 g, 2.05 mM) and Na_2CO_3 (0.6 g) were treated under nitrogen with degassed H_2O (10 ml) and degassed ethanol (5 ml). The slurry was stirred under nitrogen and green lustrous crystals formed in about 1 hour. The product was washed with 3 x 10 ml H_2O , small portion ethanol, and finally 4 x 10 ml ether. The crystals are vacuum dried and transferred and stored in an inert atmosphere box. The yield was 0.75 g (88%). The material was used without further purification.

Oxidative addition reactions of [difluoro[3,3'-trimethylene dinitrilo]di-2-pentanone dioximato borate]rhodium(I), $(\text{Rh}(\text{C}_2\text{DOBF}_2))$, with alkyl halides.

Trans-methyl Rh(C₂DOBF₂) iodide

The Rh(C₂DOBF₂) (0.1 g, 0.24 mM) was transferred to a round bottom flask in the inert atmosphere box and fitted with a rubber septum. THF (10 ml) was added and an excess of methyl iodide was injected through the septum. Immediately the red color of the Rh^I species changes to light yellow. The solvent is removed on a rotary evaporator and the solid recrystallized from either THF or CH₂Cl₂.
nmr (60 MHz in CD₂Cl₂); δ 0.2 (d, J=3Hz), δ 1.2 (t, J=8Hz), δ 2.35 (S), δ 2.8 (q, J=8Hz) δ 4.0 (M).

Anal. Calcd for RhBF₂O₂IC₁₄H₂₅N₄: C, 30.02; H, 4.50; N, 10.00.
Found: C, 29.75; H, 4.43; N, 9.39.

Trans-ethyl Rh(C₂DOBF₂)iodide

The above procedure yielded the ethyl iodide derivative as yellow crystals. nmr (60 MHz in CDCl₃); δ 0.22 (t, J=8, 3H), δ 1.13 (t on q J=8Hz, 8H), δ 2.30 (S, 6-7H), δ 4.47 (q on M, J=8Hz, 4-5H), δ 4.0 (M, 3-4H).

Anal. Calcd for RhBF₂O₂IC₁₅H₂₇N₄: C, 31.38; H, 4.74; N, 9.76.
Found: C, 32.29; H, 4.79; N, 9.42.

Trans-isopropyl Rh(C₂DOBF₂) iodide

The above procedure yielded the isopropyl iodide derivative. The product was purified by column chromatography on silica gel using CH₂Cl₂ and 20% CH₃CN/CH₂Cl₂ as eluting solvents. The product can be crystallized from either CH₂Cl₂ or THF yielding yellow crystals.

nmr (60 MHz in CDCl_3): δ 0.19 (d, $J=6\text{Hz}$, 6H), δ 1.2 (t, $J=8\text{Hz}$, 6H), δ 2.3 (s, 7H), δ 2.8 (q, $J=8\text{Hz}$, 6H), δ 4.0 (M, 4H).

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{IC}_{16}\text{H}_{29}\text{N}_4$: C, 32.68; H, 4.97; N, 9.53; Rh, 17.50; I, 21.58. Found: C, 32.01; H, 4.75; N, 9.64; Rh, 17.9; I, 21.79.

Trans n-butyl $\text{Rh}(\text{C}_2\text{DOBF}_2)$ bromide

$\text{Rh}(\text{C}_2\text{DOBF}_2)$ (0.11 g, 0.27 mM) was dissolved in 5 ml DME, and n-butyl bromide (0.03 ml, 0.3 mM) was injected through septum. The flask was wrapped in aluminum foil to protect it from light and the solution was heated to $70-80^\circ\text{C}$. After 2 hours the solution was filtered and the product crystallized from THF to yield 0.13 g (84%) of yellow crystals.

nmr (60 MHz in CDCl_3): δ 0.9-1.2 (t on M, $J=8\text{Hz}$, 15H), δ 2.4 (s, 6H), δ 2.8 (M, 6H), δ 4.0 (M, 4H).

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{17}\text{H}_{31}\text{N}_4$: C, 36.80; H, 5.63; N, 10.21; Rh, 18.53; Br, 14.40. Found: C, 37.04; H, 5.61; N, 10.12; Rh, 18.4; Br, 14.16.

Trans-sec butyl- $\text{Rh}(\text{C}_2\text{DOBF}_2)$ bromide


The above procedure yielded after 5 hours at 80°C an orange solution. Tlc (20% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) of this solution indicated a pure compound. The product was crystallized from THF. nmr (60 MHz in CDCl_3): δ 0.6 (d, $J=6\text{Hz}$), δ 1.2 (t, $J=8\text{Hz}$), δ 2.3 (s), δ 2.8 (q, $J=8\text{Hz}$), δ 4.1 (M).

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{17}\text{H}_{31}\text{N}_4$: C, 36.80; H, 5.63; N, 10.21; Rh, 18.53; Br, 14.40. Found: C, 36.83; H, 5.54; N, 10.15; Rh, 18.1; Br, 14.48.

Trans-hex-5-ene-Rh(C₂DOBF₂)bromide,  Rh(C₂DOBF₂)Br

6-bromohexene-1 (0.1 g, 0.59 mM) was added to Rh(C₂DOBF₂) (0.18 g, 0.43mM) dissolved in 5 ml DME. After 1 hour at 80° yellow crystals had formed. Gas chromatography [3 m column packed with 15% QF-1 on chromsorb w. aw. DMCS 70-80 mesh] of the solution showed there to be a very small amount of 1-hexene or methyl cyclopentane¹². The same glpc results are obtained when the reaction is carried out at room temperature and protected from light. Tlc shows only one product. The product can be recrystallized from either CH₂Cl₂/Et₂O or ethanol. The pure product does not decompose in the gas chromatograph under the above conditions. nmr (60 MHz, in CDCl₃): δ 1.07 (t on M, J=7Hz, 12H), δ 1.8 (m, 2H), δ 2.26 (S, 6H), δ 2.7 (q on m, J=7Hz, 6H), δ 4.9 (m, 4H), δ 4.66 (S, 1H), δ 4.90 (S, 1H), δ 5.2 (m, 1H). The nmr spectrum indicates a terminal olefin with proton signals at δ 4.66, 4.90 and 5.2.

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{19}\text{H}_{33}\text{N}_4$: C, 39.27; H, 5.72; N, 9.64; Br, 13.75. Found: C, 39.47; H, 5.71; N, 9.85; Br, 13.43.

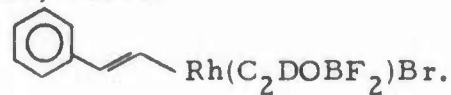
Trans-pent-4-ene Rh(C₂DOBF₂)bromide,  Rh(C₂DOBF₂)Br

The above procedure was repeated using 5-bromopentene-1 as the substrate. Glpc indicates a very small amount of cyclopentene¹².

Isolation of pure product and reinjection into gas chromatograph under identical conditions shows that the product does not decompose. The product was recrystallized from ethanol. nmr (60 MHz in CDCl_3): δ 1.17 (t on m, $J=7\text{Hz}$, 10H), δ 1.8 (m, 2H), δ 2.35 (s, 6H), δ 2.8 (q on m, $J=7\text{Hz}$, 6H), δ 4.1 (m, 4H), δ 4.71 (m, 1H), δ 4.96 (m, 1H), δ 5.3 (m, 1H). The nmr spectrum indicates a terminal olefin with proton signals at δ 4.71, 4.96 and 5.3.

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{18}\text{H}_{31}\text{N}_4$: C, 38.12; H, 5.51; N, 9.88; Br, 14.09. Found: C, 38.37; H, 5.64; N, 10.06; Br, 14.52.

Trans-trans β -(Rh(C_2DOBF_2))bromide)styrenyl,



Freshly distilled trans- β -bromostyrene (50 ml, 0.39 mM) was added to $\text{Rh}(\text{C}_2\text{DOBF}_2)$ (0.15 g, 0.36 mM) dissolved in 5 ml DME. After 22 hours at 80°C a yellow precipitate was collected and washed with Et_2O . The product was recrystallized from THF. nmr (100 MHz in CDCl_3): δ 1.21 (t, $J=8\text{Hz}$, 6H), δ 2.42 (s, 6H), δ 2.90 (q, $J=8\text{Hz}$, 4H), δ 3.8 (m, 6H), δ 5.43 (d, $J=16\text{ Hz}$, 1H), δ 6.29 (d, $J=16\text{ Hz}$, 1H), δ 7.14 (s, 5 H). The coupling constant of the olefinic proton is diagnostic of trans coupling⁸.

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{21}\text{H}_{29}\text{N}_4$: C, 42.04; H, 4.86; N, 9.31; Rh, 17.1; Br, 13.30. Found: C, 42.13; H, 5.10; N, 8.94; Rh, 16.3; Br, 12.64.

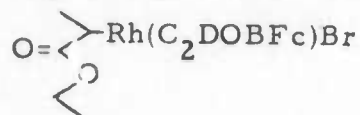
Trans-benzyl-Rh(C_2DOBF_2))bromide

Benzyl bromide (20 ml, 0.17 mM) was added to $\text{Rh}(\text{C}_2\text{DOBF}_2)$ (0.05 g, 0.12 mM) dissolved in THF. The color changed immediately

from red to yellow and crystals were obtained from the filtered THF solution. nmr (60 MHz in CDCl_3): δ 1.2 (t, $J=8$ Hz, 6H), δ 2.2 (s, 6H), δ 2.2-3.1 (d on q on m, $J_d=2$ Hz, 8H), δ 3.8 (m, 4H), δ 7.0 (m, 5H).

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{20}\text{H}_{29}\text{N}_4$: C, 40.78; H, 4.96; N, 9.51; Rh, 17.47; Br, 13.56. Found: C, 40.77; H, 5.00; N, 9.74; Rh, 17.55; Br, 13.56.

Trans-ethyl- α -propionate-Rh(C_2DOBF_2)bromide



Ethyl-2-bromopropionate (0.1 ml, 0.78 mM) was added to $\text{Rh}(\text{C}_2\text{DOBF}_2)$ (0.12, 0.29 mM) dissolved in 10 ml THF. The color changed immediately from red to light brown. The product was crystallized from THF. Tlc shows impure material even after purification by both column and preparative thin layer chromatography. ir (KBr) 1685 cm^{-1} (s, ester). nmr (60 MHz in CDCl_3) δ 0.37 (d of d, $J_{\text{Rh-H}}=1.5$ Hz, $J_d=7$ Hz) δ 1.17 (t, $J=8$ Hz), δ 1.23 (t, $J=8$ Hz), δ 1.8-2.1 (m-impurity), δ 2.40 (s), δ 2.46 (s), δ 2.90 (q, $J=8$ Hz), δ 3.6-4.3 (m). The high field set of doublets indicates that the rhodium is bonded to the α carbon but the two sets of triplets indicates two rhodium compounds.

Anal. Calcd for $\text{RhBF}_2\text{O}_4\text{BrC}_{18}\text{H}_{31}\text{N}_4$: C, 36.08; H, 5.22; N, 9.35. Found: C, 39.20; H, 5.66; N, 8.92.

Trans-4-bromo-cyclohexyl-Rh(C_2DOBF_2)bromide

Using the techniques previously described both cis-1,4-dibromocyclohexane and trans-1,4-dibromocyclohexane were treated with

$\text{Rh}(\text{C}_2\text{DOBF}_2)$ in DME. The *cis* isomer required 4-5 hours to react with the $\text{Rh}(\text{C}_2\text{DOBF}_2)$. The *trans* isomer required at least several hours longer. Both substrates yielded the same products. Preparative tlc (20% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ on silica gel) separated two compounds, $\text{Rh}(\text{C}_2\text{DOBF}_2)\text{Br}_2$ and $\text{Br}-\text{C}_6\text{H}_{10}-\text{Rh}(\text{C}_2\text{DOBF}_2)\text{Br}$. The nmr of both cyclohexyl products show a mixture of *cis* and *trans* cyclohexyl adducts and both spectra are identical. nmr (100 MHz in CDCl_3): δ 1.19 (t, $J=7\text{Hz}$), δ 1.64 (S on m), δ 2.41 (S), δ 2.85 (q, $J=7\text{Hz}$), δ 3.6-4.6 (m). $\delta_{\text{Hax}} \sim 3.80$ and $\delta_{\text{Heq}} = 4.65$ for the proton vicinal to bromine on the cyclohexyl ring^{9,10,11}. Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{Br}_2\text{C}_{13}\text{H}_{22}\text{N}_4$: Br, 27.66. Found: Br, 27.6. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{19}\text{H}_{32}\text{N}_4$: C, 34.57; H, 4.89; N, 8.49; Rh, 15.59; Br, 24.22. Found from *cis*-1,4-dibromocyclohexane reaction: C, 34.92; H, 4.89; N, 8.71; Rh, 15.9; Br, 23.35. Found from *trans*-1,4-dibromocyclohexane reaction: C, 34.42; H, 4.86; N, 8.84; Rh, 16.0; Br, 22.36.

Trans-4-methyl cyclohexyl-Rh(C₂DOBF₂)bromide

Cis-4-methyl cyclohexylbromide, prepared by the method of Eliel¹³, (0.1 g, 0.58 mM) was added to $\text{Rh}(\text{C}_2\text{DOBF}_2)$ (0.12 g, 0.29mM) dissolved in 10 ml DME. The reaction was protected from light and held at 80°C for 22 hours. Preparative tlc (silica gel, 20% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) was used to purify the product. Golden crystals were collected and washed with Et_2O . nmr (100 MHz in CDCl_3): δ 0.73 (d, $J=6\text{Hz}$), δ 0.88 (d, $J=7\text{Hz}$), δ 1.19 (t, $J=7.5\text{Hz}$); δ 1.7 (m), δ 2.38 (S), δ 2.85 (q on m, $J=7.5\text{Hz}$), δ 3.5-4.3 (m).

The two high field doublets indicate both cis and trans methyl groups¹⁴.

Anal. Calcd for $\text{RhBF}_2\text{O}_2\text{BrC}_{20}\text{H}_{35}\text{N}_4$: C, 40.36; H, 5.93; N, 9.41.

Found: C, 41.37; H, 6.16; N, 9.12.

Trans-4-methyl cyclohexyl bromide was prepared in 75% purity from a commercial cis, trans mixture of 4-methyl cyclohexyl bromide by vigorous base assisted preferential elimination of the cis isomer. The product was distilled to remove methylcyclohexene and nmr analysis indicated 75% trans-4-methylcyclohexylbromide. $\text{Rh}(\text{C}_2\text{DOBF}_2)$ was treated with the trans isomer for 31 hours at 80°. The product was isolated by preparative tlc. The nmr of the product was identical to the product obtained from the cis isomer.




Kinetic Experiments

All kinetic measurements were made on a Cary 15 spectrophotometer. The solutions were prepared in an inert atmosphere box. $\text{Rh}(\text{C}_2\text{DOBF}_2)$ in either THF or DME has absorption bands at 560 nm and 522 nm and the $\text{Rh}(\text{III})$ products have a single weak absorbance between 400 nm and 350 nm, depending on the alkyl group and the halide. All rates were determined pseudo n^{th} order by using alkyl halide in large excess (38X-462X), and the disappearance of the absorbance at 560nm was followed to about 90% of the original absorbance. When alkyl iodides were used as substrates the sample cell was attached to two syringes in such a fashion that the contents of both syringes were injected simultaneously while the cell was in the spectrometer. The mixing took about 2 seconds. Air took longer than 2000 seconds to significantly affect the reaction.

Alkyl bromides were slow enough to react that the above apparatus was not useful. The reaction with the bromides were done in the inert atmosphere box and periodically samples were taken and their spectrum measured. The curvets used (1 mm) could be stopped with well greased glass stoppers so that the sample was protected from air for more than 1 hour.

Results:

Primary iodides and bromides, and secondary bromides behave in a second order fashion. The rate law is $k_2[RX][Rh(C_2DOBF_2)]$

<u>RX</u>	$\frac{k_2}{M^{-1}sec^{-1}}$
 I	1.56 $M^{-1}sec^{-1}$
 Br	$8.55 \times 10^{-3} M^{-1}sec^{-1}$
 Br	$3.38 \times 10^{-5} M^{-1}sec^{-1}$

Secondary iodides give a strange empirical rate law:

$k[RI]/[Rh(C_2DOBF_6)]^{1/2}$. This rate law was observed for isopropyl iodide and 2-bromooctane over a concentration range of 43 to 462 fold excess of the secondary iodide. At present no reasonable explanation can be inferred from this rate law.

Summary

The question of the mechanism of oxidative addition in this particular system has been explored. Primary iodides and bromides and secondary bromides react with $\text{Rh}(\text{C}_2\text{DOBF}_2)$ in a way that suggests nucleophilic displacement of the halide. The rate law and the rate constants support this. However, a vinyl bromide reacts with retention of geometry about the double bond and the cyclohexyl systems lose their stereochemistry, indicating that a pure $\text{S}_{\text{N}}2$ reaction is not taking place. It was found that galvinoxyl¹⁵, a radical trap for carbon and oxygen radicals, did not inhibit reaction of either primary or secondary iodides or bromides. The absence of carbon radicals is further supported by failure to find significant amounts of methylcyclopentane when 6-bromohexene-1 was treated with $\text{Rh}(\text{C}_2\text{DOBF}_2)$.

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RESEARCH REPORT

Rex Stark

September 1973

Introduction

In my last report I discussed the possibility of metal-metal bond formation via redistribution reactions of the transition metal complexes of the group IV metals. Additional work has shown this to be an impractical method since the reactions were found to be quite slow and usually resulted in intractable mixtures of products in low yields accompanied by some decomposition.

Current research efforts involve the $\text{Rh}(\text{DO})(\text{DOH})$ and related compounds previously detailed by Don Murphy^{1,2,3}. Attempts at making additional transition metal derivatives were for the most part unsuccessful. Unexpected problems developed in making simple germanium derivatives. Present studies of sulfur compounds of the rhodium system have yielded some promising results.

The $\text{Rh}(\text{DO})(\text{DOH})$ System

The compounds $\text{Rh}(\text{DO})(\text{DOH})\text{Cl}_2$ ², $\text{Rh}(\text{DO})(\text{DOH})$ ², $\text{MeRh}(\text{DO})(\text{DOH})\text{I}$ ³, $\text{Rh}(\text{DO})(\text{DOBF}_2)\text{Cl}_2$ ³, and $\text{Rh}(\text{DO})(\text{DOBF}_2)$ ³ were prepared as reported by Don Murphy. The previously unreported $\text{MeRh}(\text{DO})(\text{DOBF}_2)\text{I}$ was prepared and isolated by preparative TLC.

Group IV Derivatives

$\text{Ph}_3\text{SnRh}(\text{DO})(\text{DOH})\text{Cl}$ was easily prepared from $\text{Rh}(\text{DO})(\text{DOH})$ and Ph_3SnCl in THF². Reduction of this compound with Na/Hg and treatment

with Ph_3SnCl leads to the bis-triphenyltin derivative, but use of Ph_3GeBr led to a dark air sensitive mixture from which only crude products were recovered.

Addition of Ph_3GeBr to $\text{Rh}(\text{DO})(\text{DOBF}_2)$, 1, in THF led to a mixture of several components including a large amount of $\text{Rh}(\text{DO})(\text{DOBF}_2)\text{Br}_2$. The reaction was slow, and some unreacted 1 was present.

The reaction of 1 with Ph_3GeCl was also slow. After two days the rhodium products were separated and found by nmr to contain no aryl. The mixture included a large amount of $\text{Rh}(\text{DO})(\text{DOBF}_2)\text{Cl}_2$.

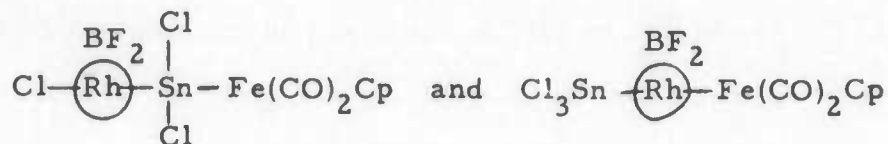
Addition of Ph_3SnCl to 1 in THF gave the expected $\text{Ph}_3\text{SnRh}(\text{DO})(\text{DOBF}_2)\text{Cl}$, but several recrystallizations were necessary for reasonable purity. The product is air sensitive in solution.

1 reacted quickly with excess Ph_2SnCl_2 in THF to give a mixture of products. The major product isolated was found to contain much more chlorine than the expected $\text{ClPh}_2\text{SnRh}(\text{DO})(\text{DOBF}_2)\text{Cl}$. This product has not been identified.

In THF solution the reaction of 1 with Ph_3SnH was fast, and led to a crude air sensitive mixture. The infrared spectrum indicated no Sn-H or Rh-H.

Transition Metal Complexes

The addition of $\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$ to 1 in THF was reported³ to go rapidly to a blue-black intermediate, followed by separation of the orange product. This work was repeated and the product was isolated in pure form, but its identity still has not been established. The possible products are



The analogous system using $\text{Cl}_3\text{SnMn}(\text{CO})_5$ gave unexpected results. The initial addition in THF led to a blue-black solution which remained as such for several days. A blue-black hygroscopic solid was isolated which gave an inconclusive analysis. Conductivity studies may indicate if the isolated compound is a stable ionic intermediate.

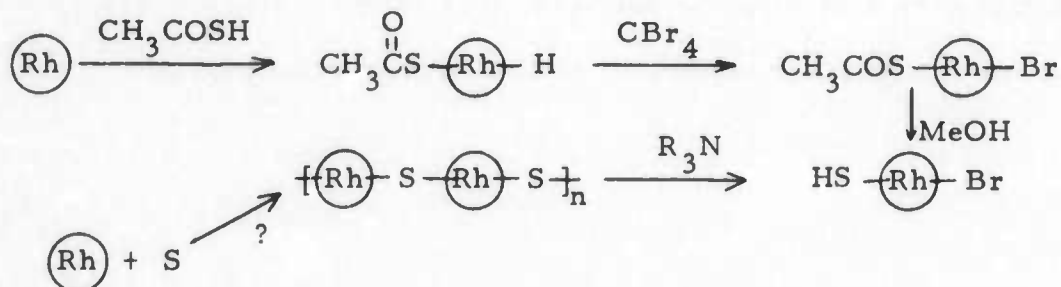
$\underline{1}$ was treated with $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ in THF. The reaction was very slow and workup of the products led to recovery of significant amounts of both starting compounds. Another dark unidentified solid was shown by IR to contain no CO.

Reaction of $\underline{1}$ with $\text{ClPh}_2\text{SnMn}(\text{CO})_5$ yielded only crude products, including unreacted $\underline{1}$.

Sulfur Containing Compounds

Preliminary studies are underway in the use of sulfur (or possibly selenium or tellurium) as a connecting atom in the rhodium DOH system. Heavy metal sulfides are known to have strong covalent bonds, and may allow for functionalization or coupling involving the sulfur end of the molecule without destroying the Rh-S bond.

The reaction sequence initially considered in our group was the following:

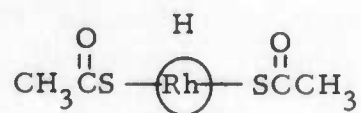
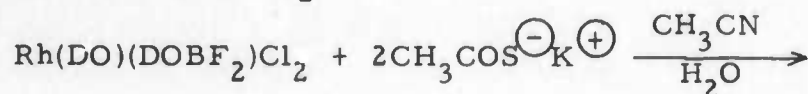


Addition of CH_3COSH to 1 in THF led to a red solution from which a red-brown solid was isolated. Infrared indicated a strong acyl band but no Rh-H. Some unreacted 1 was also recovered. The expected facile oxidative addition of MeCOSH thus does not occur.

Reaction of 1 with one equivalent of Se metal gave a dark solution containing much unreacted 1. Apparently an excess of S or Se should be used in these one-step polymerization attempts.

Potassium thioacetate was prepared by slightly modifying the literature method⁴. The salt is very hygroscopic and also air sensitive, readily changing from white to a salmon color. Lithium thioacetate was prepared from MeCOSH and Li_2CO_3 .

Reaction of $\text{Rh}(\text{DO})(\text{DOBF}_2)\text{Cl}_2$ with excess MeCOSK in acetonitrile-water gave the desired bis-thioacetate but with an unexpected modification. The product was isolated by preparative TLC and shown to have the oxime bridge rather than BF_2 .

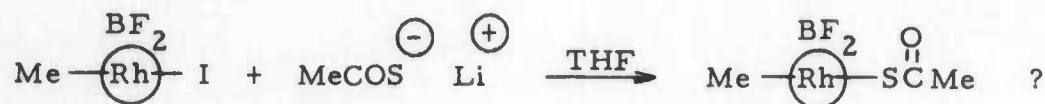


This destruction of the BF_2 bridge by water was unexpected, though Mike MacLaury had an earlier problem upon recrystallizing one of his products from ethanol. Considering the insolubility of potassium thioacetate in even polar organic solvents, it is expected that the sodium or lithium salts might fare better. It is also apparent that organic

solvents used, in this case acetonitrile, must be dried. The reaction of $\text{Rh}(\text{DO})(\text{DOBF}_2)\text{Cl}_2$ with CH_3COSLi in undried CH_3CN gave an apparent mixture of the BF_2 and oxime bridged species.

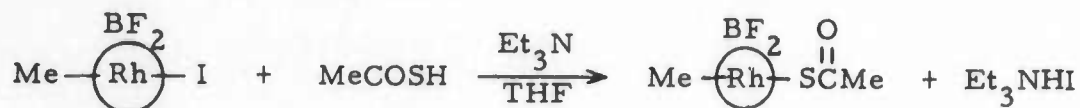
Reaction of the oxime bridged dichloride $\text{Rh}(\text{DO})(\text{DOH})\text{Cl}_2$ with excess CH_3COSLi in acetonitrile-water gave anomalous results. The major product was yellow and water soluble, having $R_f = 0$ on silica with acetonitrile. This product showed no acyl on the rhodium. This work will be repeated.

The desirability of having the mono-thioacetate and the availability of $\text{MeRh}(\text{DO})(\text{DOBF}_2)\text{I}$ prompted the following synthesis attempt.

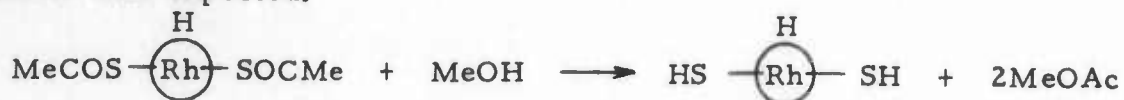


Done on a micro scale, TLC of the products indicated seven components, the two major ones being the BF_2 and oxime bridged species. Addition of water converted the BF_2 to the oxime. This work will be repeated on a preparative scale.

Initial attempts to make the above mono-thioacetate by the following method were unsuccessful and gave incomplete reaction.



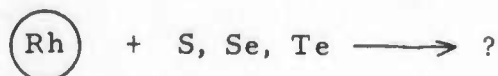
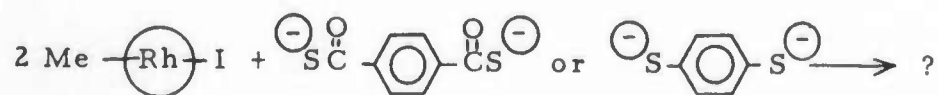
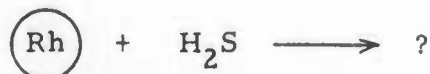
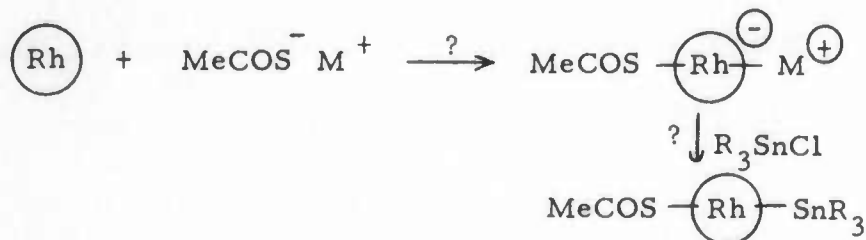
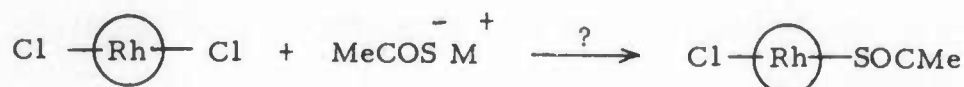
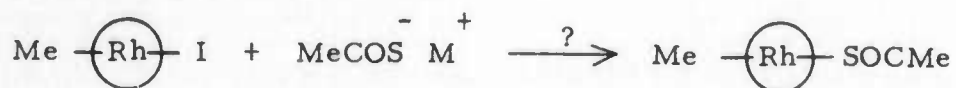
Methanolysis of the rhodium thioacetates was found to be more difficult than expected.



The reactions were done on a small scale, with MeOAc being looked for by vpc. Adding excess methanol to a dichloromethane solution of the bis-thioacetate gave no methyl acetate after 24 hours. Addition of NaOMe to the solution gave no MeOAc after another 24 hours. In methanol with no other solvent, no reaction occurred. In THF solution with a large excess of methanol there was no reaction after 8 hours, and TLC indicated only starting material. Adding a trace of NaOMe turned the solution dark and MeOAc was observed in large quantity, though evaporation of the solvent made quantitative calculations difficult. This work will be scaled up and repeated.

Future Work

Proposed syntheses include the following, using either the BF_2 or oxime bridged compounds.



In addition: possible work on the cobalt DOH system; further attempts to incorporate germanium into the DOH system; possible modifications of the BF_2 bridge to BR_2 or BAR_2 to increase solubility.

Experimental

Starting materials in the rhodium DOH system were made as earlier described^{1,2,3}. Commercial thioacetic acid was found to contain large amounts of acetic acid, which was removed by repeated distillations.

Preparative TLC was done on 2000 μ Sil Gel GF.

$\text{MeRh}(\text{DO})(\text{DOBF}_2)\text{I}$

$\text{Rh}(\text{DO})(\text{DOBF}_2)$ (1, 250 mg, .64 mmole) was suspended in 5cc THF. Excess methyl iodide (.8 mmole, ~50 μ l) was added by syringe. An orange solid precipitated after a few minutes. The mixture was stirred 3 hours, the solid collected and washed once with cold THF. A second crop was collected, and the product was purified by prep TLC in 20% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. Yield 286 mg. (84%). Analysis. Calculated for $\text{C}_{12}\text{H}_{21}\text{BF}_2\text{IN}_4\text{O}_2\text{Rh}$: C, 27.1; H, 3.98; N, 10.5. Found: C, 27.42; H, 4.06; N, 10.76.

$\text{Ph}_3\text{SnRh}(\text{DO})(\text{DOBF}_2)\text{Cl}$

A suspension of 1 (100 mg, .26 mmole) in 5cc THF was treated with Ph_3SnCl (150 mg, .39 mmole) in THF. An orange solid formed after a few moments. The solid was filtered after one hour and washed with THF. Crude yield 167 mg. (84%). The product was crystallized several times from CH_2Cl_2 /hexane. Analysis. Calculated for $\text{C}_{29}\text{H}_{33}\text{BClF}_2\text{N}_4\text{O}_2\text{RhSn}$: C, 44.9; H, 4.3; N, 7.23. Found: C, 43.75; H, 4.59; N, 7.84.

Attempted Preparation of $\text{ClPh}_2\text{SnRh}(\text{CO})(\text{DOBF}_2)\text{Cl}$

A suspension of 1 (100 mg, .26 mmole) in THF was treated with Ph_2SnCl_2 (150 mg, excess) in THF. The solution turned orange immediately and a lustrous precipitate formed. After stirring overnight the solid dissolved. The solution was evaporated and the solid crystallized from THF/hexane. Yield 90 mg. The product was triturated with hexane to remove traces of Ph_2SnCl_2 . Recover 60 mg.

Analysis. Calculated for $\text{C}_{23}\text{H}_{28}\text{BCl}_2\text{F}_2\text{N}_4\text{O}_2\text{RhSn}$: C, 37.63; H, 3.84; N, 7.63; Cl, 9.66. Found: C, 33.84; H, 3.76; N, 6.67; Cl, 13.01.

Product has not been identified.

Reaction of 1 with $\text{Cl}_3\text{SnMn}(\text{CO})_5$

A suspension of 1 (200 mg, .52 mmole) in THF was treated with $\text{Cl}_3\text{SnMn}(\text{CO})_5$ (231 mg, .55 mmole) in THF. A blue-black solution formed which remained so for two days. The solution was filtered under inert atmosphere to yield ~.1 gm blue solid. An aliquot of the filtrate turned first purple and then orange when exposed to air.

Evaporation of the filtrate yielded ~.3 gm blue solid. This was crystallized from THF/hexane to .2 gm hygroscopic blue-black powder.

Analysis. Calculated for $\text{C}_{16}\text{H}_{18}\text{BCl}_3\text{F}_2\text{MnN}_4\text{O}_7\text{RhSn}$: C, 23.7; H, 2.25; Cl, 13.13. Found: C, 22.71; H, 2.68; Cl not done. Compound is unidentified at this time.

Potassium Thioacetate⁴

Thioacetic acid (1.0 gm, .94 cc, 13.14 mmole) was dissolved slowly in ice cold aqueous KOH (.715 gm, 12.75 mmole). The clear solution was stripped and the resulting white solid placed in a vacuum desiccator.

Thioacetic Acid and 1

A suspension of 1 (100 mg, .26 mmole) in 5 cc THF was treated with a slight excess of MeCOSH. After 10-15 minutes a deep red solution formed, which was filtered and evaporated to a red-brown solid. About 25 mg 1 was recovered from the frit. The red-brown solid was somewhat air sensitive, and IR indicated acyl but no Rh-H.

(MeCOS)₂Rh(DO)(DOH)

A solution of Rh(DO)(DOBF₂)Cl₂ (200 mg, .434 mmole) in acetonitrile was added to solid potassium thioacetate (.5 gm, 4 mmole), and degassed water was added until the solution cleared. After stirring three hours the solution was evaporated and the residues separated by TLC in 50% CH₃CN/CH₂Cl₂. Yield 137 mg (64%). IR shows strong acyl at 1620-1630 cm⁻¹. BF₂ bridge gone, other bands indicative of oxime. NMR (60 MHz in CDCl₃): 129 cps (S, 6H, acyl); 139, 142 cps (D, 12H, ligand methyls); 140 cps (M, 2H, methylene) and 240-250 cps (T, 4H, methylenes). Analysis. Calculate for C₁₅H₂₅N₄O₄RhS₂: C, 36.6; H, 5.13; N, 11.4. Found: C, 36.03; H, 4.87; N, 11.96.

Lithium Thioacetate

Thioacetic acid (2 gm, 1.88 cc, 26.28 mmole) was added slowly to an ice cold aqueous solution of Li₂CO₃ (.887 gm, 12 mmole). The solution was evaporated to dryness and the resulting solid stored in a vacuum desiccator.

MeRh(DO)(DOBF₂)I and Lithium Thioacetate

The methyl iodide complex (10 mg, 1.9×10^{-5} mole) and lithium thioacetate (10-20 mg, excess) were mixed dry and THF was added. A yellow solution slowly formed and after two hours all the solid had dissolved. TLC of the solution indicated seven components, the major ones being the methyl iodide complex and apparently the oxime and BF₂ bridged products. Addition of 1cc H₂O and stirring for three days resulted in only the proposed oxime bridged product and traces of several other compounds being present. The reaction is apparently quite slow.

Methanolysis of (MeCOS)₂Rh(DO)(DOH)

The bis-thioacetate (4.9 mg) was placed in .1 ml THF and 40 μ l MeOH was added. After stirring 8 hours no MeOAc was visible by vpc, and TLC indicated only starting material. Addition of 40 μ l MeOH and a trace of NaOMe turned the suspension dark orange, and everything dissolved instantly. A deep red solution quickly developed, and a large amount of MeOAc was observed.

References

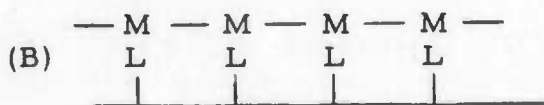
- (1) New Superconductors: First Semi-Annual Technical Report, Center for Materials Research, Stanford University, 1971.
- (2) New Superconductors: Third Semi-Annual Technical Report, Center for Materials Research, Stanford University, 1972.
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RESEARCH REPORT
Surface-Bound Metal Clusters
Howard Heitner
August 1973

The object of this project was to synthesize metal clusters bound to polymer surfaces. In general the structures of known metal cluster complexes are closed polyhedra. If, however, the metal atoms prior to cluster formation are bound to ligands chemically bonded to a polymer surface (A), a reaction such as a reduction reaction might produce a metal



complex whose conformation follows the disposition of ligands on the polymer surface (B).



Such a cluster would have either the form of a linear or branched chain or a two dimensional sheet of metal atoms. Such a substance might be a superconductor of the phonon type. Because the conductor would be essentially an atomic monolayer magnetic properties would be different from a bulk superconducting metal.

Types of Reactions Used

Two principal types of reactions were used to produce cluster compounds. The first was reduction of metallic halides bonded to surface ligands. The

second was the initial attachment of metal complex containing sulfur, followed by reaction with a second metal compound. The object here was the formation of a sulfur bridged metal cluster.

Supports

The polymeric support used in this work was silica gel. The surface siloxyl group SiOH can react with alkoxyl silanes containing ligand groups. The general approach was the same as that for silica supported homogeneous catalysts.¹ Initially work was done with Cabosil, a finely divided silica produced by high temperature hydrolysis of SiCl_4 . However this material was impossible to filter in glass frits. Cabosil could be pressed into pellets or flakes, however it was found that reactant solutions did not diffuse readily through them. Most of the work was done on Davison Type 62 silica gel which has a surface area of $340 \text{ m}^2/\text{gm}$ and an average pore diameter of 140 \AA . (This technical information provided by the vendor was not checked). Using the figure of Hockey² of 1.4 reactive SiOH groups per 100 \AA this corresponds to 7.9×10^{-4} moles of reactive SiOH per gram of silica.

Ligands

Dimethylethoxymercaptoethylsilane was synthesized by the literature³ method from thiolacetic acid and vinyl dimethylethoxysilane. 3-amino-propyltriethoxysilane and 3-mercaptopropyltrimethoxysilane were purchased from Aldrich. In initial experiments with dimethylethoxymercaptoethylsilane the ligand was attached by refluxing the ligand in dry xylene with silica gel. Initial experiments gave considerable variation in sulfur analyses (0.71 to 2.43). In addition reaction of this metal with AgNO_3

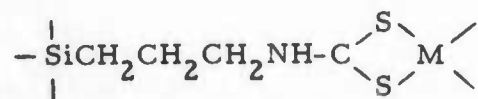
and $\text{Pb}(\text{NO}_3)_2$ gave black colors. It is possible that this compound decomposes thermally.



The SiSH group hydrolyzes readily to give sulfide ion.

In another initial experiment ethyl phosphite was reacted with silica gel to give a phosphorus content of up to 1.40%. However this material was not used because it is very water sensitive.

(3-mercaptopropyl)trimethoxysilane was reacted with Davison silica gel by stirring it in excess, in dry benzene for several days with a small amount of di-*i*-propyl amine. The sulfur content was 2.24% which corresponds to 90% reaction of the available SiOH groups. This material did not give a black color with Pb^{+2} . Its reactivity was uniform from batch to batch. The 3-aminopropyl triethoxysilane was reacted in a similar manner without added amine. This material was not analyzed because of the low absolute amount of N present. The amino silica could be readily reacted with CS_2 in ethanol in the presence of metal salts to give deeply colored substances which presumably were attached via one or more dithiocarbamate linkages.



This reaction was observed for the following metals Fe, Co, Ni, Rh, Ir, Au and Pb. Presumably the list is even more extensive.

Reduction Experiments

The following Table I is a tabular summary of reductions done on silica bound metals. It was hoped to examine the products by ESCA, but since an instrument was not available no ESCA was done. The reduced products were examined in some cases by X-ray diffraction in an effort to detect metal crystals. None were found. As a control, a sample of Pt on silica was examined (0.8% Pt). It showed weak Pt lines. The limit of detection of this method is about 50 Å so the presence of smaller metal crystals cannot be ruled out. Analyses unless otherwise indicated were done by electron microprobe. A comparison of this method with atomic absorption was done with the following results.

<u>Element</u>	<u>A. A.</u>	<u>Microprobe</u>
Ki.	0.75	0.67
Rh	0.917	0.806
Rh	0.157	0.11
P	0.38	0.540
Cr	0.48	0.34
Cr	0.60	0.37

Cluster Syntheses

Since ESCA was unavailable during the period of this work and most other spectroscopic tools could not be applied to this problem, chemical analysis was used to detect cluster formation. The basic technique was to saturate the surface ligands with one complex and then by some set of reactions introduce another metal. If the product showed roughly

Table I. Reduction of Metal Complexes on Silica

Sample	Ligand	Metal	Reductant	Remarks and Analysis
20-2	-NH ₂	Cr	--	0.66% Cr by A.A.
21-1	-NH ₂	Cr	Fluorenone Ketyl	0.48% Cr by A.A., yellow
22-1	-NH ₂	Re(Re ₃ Br ₉)	--	black, no analysis
22-1	-NH ₂	Re	NaBH ₄ in DMF	brown
24-3	-NH ₂	Nb	--	yellow, 3.6% Nb
25-3	-NH ₂	Nb	(i-butyl) ₂ AlH	air sensitive, 4.85% Nb, 2.11% Al**
27-1	-SH	Rh	--	red, 5.12% Rh
27-2	-SH	Rh	(i-butyl) ₂ AlH	black, air sensitive 4.37% Rh, 3.50% Al
28-1	-SH	Ir	EtOH?	possible reduction by EtOH**
28-3	-SH	Pb	--	3.42% Pb, yellow
28-4	-SH	Pb	(i-butyl) ₂ AlH	3.50% Pb, 1.74% Al**
28-5	-SH	Rh(DMF)	--	0.85% Rh, yellow
29-1	-SH	Rh	(i-butyl) ₂ AlH	0.77% Rh, 2.50% Al**
31-1	-SH	Au	--	only trace Au
31-2	-SH	Au	H ₂	only trace Au**

Following samples were prepared but no reduction performed.

44-1	$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ -\text{C}-\text{N}-\text{C}-\text{Rh} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$	4.67% Rh, red-brown, 1.92% S
45-1	$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ -\text{C}-\text{N}-\text{C}-\text{Au} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$	4.20% Au, brown, 0.235% S

**X-ray amorphous

equal amounts of both metals as well as an increased amount of the bridging ligand element (sulfur) it was possible that a cluster was being formed. The following is a tabular summary of this work.

Table II. S-Bearing Cluster Syntheses

Synthesis	Analytical Results
<p>(39-2)</p> $\text{Co}_2(\text{CO})_8 + \text{---SH} \rightarrow (1)$ <p>(1) + benzyldisulfide \rightarrow (2)</p> <p>(2) + $\text{Fe}_3(\text{CO})_{12} \rightarrow (39-2)$</p>	<p>Fe 2.57% Co 2.80% S 2.16%</p> <p>Possible Fe-Co-S cluster however $\text{Co}_2(\text{CO})_8$ not pure.</p>
<p>(46-1)</p> $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ -\text{C}-\text{N}-\text{C}-\text{Fe} \\ \diagdown \quad \diagup \\ \text{S} \end{array} + \text{Cr}(\text{CO})_6 \rightarrow (46-1)$	<p>Fe 13%(?) S 0.69% Cl 5.15%</p> <p>Cr 0.131%. No cluster formation.</p>
<p>(46-3)</p> $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ -\text{C}-\text{N}-\text{C}-\text{Fe} \\ \diagdown \quad \diagup \\ \text{S} \end{array} + \begin{array}{c} \text{MeNH}_2 \\ +\text{CS}_2 \end{array} \rightarrow 46-2$ <p>46-2 + $\text{Co}_2(\text{CO})_8 \rightarrow 46-3$</p>	<p>Fe 2.37% S 1.72% Cl 1.16% Co 3.5%</p> <p>Possible cluster formation $\text{Co}_2(\text{CO})_8$ sublimed.</p>
<p>(49-1)</p> $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ -\text{NH}-\text{C}-\text{Pb} \\ \diagdown \quad \diagup \\ \text{S} \end{array} + \text{ammonium polysulfide} \rightarrow 49-1$	<p>Showed crystals under E. M.</p> <p>Gave PbS diffraction pattern (X-ray)</p>

Miscellaneous Experiments

Tests for Active H₂

As a test for rhodium metal in a reduced rhodium sample (27-2) it was mixed with WO₃ and water and exposed to hydrogen. No color change was observed. A control sample of Rh on alumina turned blue rapidly. A sample (MT-48-2) of Rh₄(CO)₁₂ on phosphinated silica (obtained from M. Takeda) gave a blue color. Reduction of WO₃ to blue tungsten bronze could also be accomplished by Rh(Ø₃P)₃Cl in benzene at 4 atm after several days. This indicates that a positive test (blue color) does not necessarily indicate a metallic catalyst.

Model Systems for Reduction

Cobalt and rhodium salts were rapidly reduced to metal (confirmed by X-ray diffraction) by NaBH₄ in solution. In the presence of excess (EtO)₃P no metal was formed. The products (36-1, 37-1-3) were not identified. The rhodium product was water soluble, the cobalt products were not. These materials were not investigated extensively. The only one analyzed have a Co/P ratio of 4.72 indicating a possible cluster compound.

Conclusions

It is likely that some of the materials synthesized contained metal clusters. Further synthetic efforts should be monitored by better methods than that employed in this study. In particular ESCA is of great potential value here. The use of model systems (such as those described under miscellaneous) to study potential cluster formation is probably not worthwhile

because the complexes formed by ligands bound to surfaces and found in solution are likely to be different. Blanks with ordinary silica should be run for most of the reactions used to form clusters, to detect the precipitation of small amounts of material in cavities. This is of particular importance if chemical analysis and catalytic properties are being used as investigative tools.

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IV. EXPERIMENTAL SECTION

Collection and Reduction of the X-ray Data

Everly Fleischer

Crystals of Rh(Do)(DOH) were supplied by Dr. J. P. Collman in coordination with studies in progress in that laboratory. Precession photographs of the h0l, hk0, h1l, hk1, and hk2 zones established the crystals as belonging to monoclinic symmetry. The observed systematic absences (0k0, $k=2n+1$; h0l, $h=2n+1$) are consistent with the space group $C_{2h}^5 - P2_1/C$. The monoclinic lattice parameters were obtained from the precession photographs and refined by a least-squares refinement^A of the setting angles, χ , ϕ , and 2θ , for twelve individually centered reflections using a Picker four-circle x-ray diffractometer. The unit cell constants (at 21° C., MoK $_{\alpha 1}$) thus obtained are $a=6.962(11)$, $b=1587(3)$, $c=13.41(2)$, and $\beta=62.83(5)^\circ$. The density of 1.75 g/cm³ calculated on the basis of four formula units per cell agrees reasonably well with the density of 1.68 g/cm³ obtained by floatation in a solution of chloroform and dibromomethane.

Diffraction data were collected with a near rectangular crystal of dimensions 0.65 x 0.23 x 0.15 mm mounted in a glass capillary parallel to the longest dimension. The data were collected on a Picker automatic diffractometer by use of procedures described elsewhere.^{B, C} A take-off angle of 1.6° was employed. The diffracted beam was filtered through 3.0 mm Nb foil. The counter aperture was 5 x 5 mm square and was positioned 38 cm from the crystal. The pulse-height analyzer was set to admit approximately 95% of the MoK $_{\alpha}$ peak. Intensity data were collected using the $\theta - 2\theta$ scan method using a scan range of 0.56 to 0.52° about the peak for reflections with $2\theta \leq 35^\circ$ with allowances made

$K_{\alpha_1} - K_{\alpha_2}$ split at values higher than 35° . The scan rate was 1° per minute, and stationary background counts of 20 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded 10,000 counts/sec; however, only five reflections required attenuators. Three reflections chosen to lie in different regions of reciprocal space were monitored at regular intervals during the data collection. An overall decrease in the intensity of these standards of 11% was noted during the data collection. This decrease could be approximated as a reasonably linear function of the time of exposure of the crystal to the x-ray beam. A scaling was made to correct for this decrease. A total of 1983 reflections were collected with $2\theta \leq 45^\circ$. The data were corrected for background and Lorentz-polarization by the usual methods.^{B, C} From calculation of the absorption coefficient, no correction for absorption was deemed necessary. The p factor in the expression

$$\sigma(I) = [C + 0.25 (t_c/t_b)^2 (B_1 + B_2) + (pI)^2]^{1/2}$$

was assigned the value of 0.05. From counting statistics, 1526 of the 1983 independent reflections were above background by more than three standard deviations and thus judged observed.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct application of Patterson, Fourier, and least-squares methods. All least-squares refinements were carried out on F , minimizing the function $\sum w (|F_o| - |F_c|)^2$. The weights, w , were initially taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factor for Rh was taken from

Cromer and Waber,^D that for H from Stewart, Davidson, and Simpson,^E and all others from the appropriate tabulation.^F The structure factor calculations for F_c include allowance for anomalous scattering for Rh, the value of which were taken from the tabulation of Cromer.^G Only the 1526 independent intensities were used in the refinement of the structure.

Initially, the Rh atom was assigned an isotropic thermal parameter. Least-squares refinement of the positional and thermal parameters and a scale factor yielded the agreement factors $R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right| = 0.276$ and $R_2 = [\Sigma w (\left| F_o \right| - \left| F_c \right|)^2 / \Sigma w \left| F_o \right|^2]^{1/2} = 0.343$. Positional parameters for the eleven carbons, four nitrogens, and the two oxygen atoms were obtained, and all eighteen nonhydrogen atoms were then refined with anisotropic thermal parameters. In the final stages of refinement, the eighteen hydrogen atom positions were calculated based upon a trigonal arrangement ($C-H = 1.08 \text{ \AA}$) and included. A virial weighting scheme, $\sigma_{F_o} = A + B \left| F_o \right| + C \left| F_o \right|^2$, was also used with $A = 1.023$, $B = 0.0052$ and $C = 0.0003$. The last cycle of least-squares refinement converged to $R_1 = 0.036$ and $R_2 = 0.047$ with the largest parameter shift equal to 0.30σ . A final difference Fourier map showed no peak higher than $0.42e \text{ \AA}^{-3}$ with a $\sigma(\Delta\rho)$ of $0.13 e \text{ \AA}^{-3}$.

The atomic positional and thermal parameters for all non-hydrogen atoms derived from the last cycle of least-squares refinement are listed in Table I along with the associated standard deviations. Intramolecular distances and angles are tabulated in Tables II and III, respectively. A table of observed and calculated structure factors is available.^H

Table I: Atomic Positional and Thermal Parameters^a

Atom	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.18145(7)	0.22552(3)	-0.20805(4)	0.01924(16)	0.00239(2)	0.00466(4)	-0.00027(4)	0.00329(6)	0.00049(2)
N(1)	0.3179(8)	0.2058(3)	0.2219(4)	0.0211(16)	0.0036(2)	0.0049(4)	0.0013(5)	0.0042(7)	-0.0009(2)
N(2)	0.3012(8)	0.3531(3)	0.2319(4)	0.0205(15)	0.0031(2)	0.0046(4)	-0.0003(5)	0.0044(7)	0.0000(2)
N(3)	0.0440(8)	0.3432(3)	0.3665(4)	0.0201(15)	0.0033(2)	0.0050(4)	-0.0006(5)	0.0046(6)	-0.0009(2)
N(4)	0.0655(8)	0.1862(3)	0.3502(4)	0.0227(16)	0.0029(2)	0.0042(4)	-0.0014(5)	0.0028(7)	-0.0003(2)
O(1)	0.0954(8)	0.1031(3)	0.3346(4)	0.0355(17)	0.0025(2)	0.0083(4)	-0.0020(5)	0.0079(7)	-0.0004(2)
O(2)	0.3127(8)	0.1196(3)	0.2248(4)	0.0322(16)	0.0028(2)	0.0088(4)	0.0013(4)	0.0068(7)	-0.0019(2)
C(1)	-0.4698(12)	0.1998(5)	0.1168(6)	0.024(2)	0.0078(5)	0.0057(5)	0.0052(8)	0.0053(9)	-0.0013(4)
C(2)	0.4151(11)	0.2443(4)	0.1720(5)	0.0192(18)	0.0051(3)	0.0038(4)	0.0015(7)	0.0037(8)	-0.0006(3)
C(3)	0.4018(10)	0.3376(4)	0.1776(5)	0.0185(17)	0.0043(3)	0.0043(4)	-0.0008(6)	0.0043(8)	-0.0001(3)
C(4)	-0.5037(13)	0.3911(6)	0.1203(6)	0.032(3)	0.0078(5)	0.0068(5)	-0.0025(9)	-0.0087(11)	0.0004(5)
C(5)	-0.1371(12)	0.1463(6)	0.4527(6)	0.030(2)	0.0074(5)	0.0070(6)	-0.0051(9)	0.0070(10)	0.0002(4)
C(6)	-0.0403(10)	0.2075(4)	0.4046(5)	0.0214(19)	0.0040(3)	0.0044(5)	-0.0018(6)	0.0040(8)	-0.0001(3)
C(7)	-0.0519(10)	0.3012(4)	0.4132(5)	0.0184(18)	0.0044(3)	0.0045(4)	-0.0003(6)	0.0028(8)	-0.0013(3)
C(8)	-0.1719(11)	0.3378(5)	0.4701(6)	0.024(2)	0.0078(5)	0.0065(6)	0.0010(8)	0.0072(9)	-0.0013(4)
C(9)	0.0572(12)	0.4362(4)	0.3673(6)	0.031(2)	0.0032(3)	0.0100(6)	0.0011(7)	0.0101(11)	-0.0016(4)
C(10)	0.2570(11)	0.4664(4)	0.3587(6)	0.028(2)	0.0025(2)	0.0074(5)	-0.0007(6)	0.0064(9)	-0.0009(3)
C(11)	0.2639(12)	0.4528(4)	0.2477(6)	0.032(2)	0.0027(3)	0.0074(6)	-0.0008(7)	0.0068(10)	-0.0001(3)

^a Numbers in parentheses in all tables as well as the text are estimated standard deviations in the least significant figures.

^b The form of the anisotropic thermal ellipsoid is $\exp [-(\beta_{11}^2 h^2 + \beta_{22}^2 k^2 + \beta_{33}^2 l^2 + 2\beta_{12}^2 hk + 2\beta_{13}^2 hl + 2\beta_{23}^2 kl)]$.

Table II: Intramolecular Bond Distances (Å)

Rh-N(1)	1.951(5)
Rh-N(2)	1.987(5)
Rh-N(3)	1.999(5)
Rh-N(4)	1.952(5)
N(1)-O(1)	1.367(7)
N(4)-O(2)	1.369(7)
N(1)-C(2)	1.305(9)
N(2)-C(3)	1.287(8)
N(2)-C(11)	1.479(8)
N(3)-C(7)	1.293(8)
N(3)-C(9)	1.478(8)
N(4)-C(6)	1.300(8)
C(2)-C(3)	1.489(10)
C(6)-C(7)	1.496(9)
C(6)-C(5)	1.489(10)
C(7)-C(8)	1.489(9)
C(2)-C(1)	1.498(9)
C(3)-C(4)	1.488(10)
C(9)-C(10)	1.527(10)
C(10)-C(11)	1.526(10)

Table III: Selected Intramolecular Bond Angles (DEG)

N(1)-Rh-N(2)	79.1(2)
N(2)-Rh-N(3)	101.8(2)
N(3)-Rh-N(4)	78.9(2)
N(4)-Rh-N(1)	100.2(2)
O(2)-N(1)-C(2)	120.6(5)
O(1)-N(4)-C(6)	120.2(5)
Rh-N(1)-C(2)	118.1(5)
Rh-N(4)-C(6)	119.1(4)
Rh-N(1)-O(2)	121.3(4)
Rh-N(4)-O(1)	120.6(4)
Rh-N(2)-C(3)	116.6(4)
Rh-N(3)-C(7)	115.9(4)
Rh-N(2)-C(11)	119.2(4)
Rh-N(3)-C(9)	120.4(4)
N(2)-C(11)-C(10)	111.3(5)
C(11)-C(10)-C(9)	118.3(6)
C(10)-C(9)-N(3)	111.7(5)

DESCRIPTION OF THE STRUCTURE

The features of the molecular configuration of the complex [3, 3'-(trimethylenedinitrilo)-di-2-butanone dioximate]rhodium(I) are shown in Figure 1. In the coordination sphere of the rhodium atom are the four nitrogen atoms of the macrocyclic ligand, the bond lengths found being normal. It is well to mention that this ligand is capable of expanding to accommodate a metal the size of the rhodium ion. It is found that the Co - N bond distances in the complex, $[\text{Me}(\text{H}_2\text{O})\text{Co}(\text{DO})(\text{DOH})\text{pn}]\text{ClO}_4$,^I average 0.11 \AA shorter than those found in the complex under study, as is consistent with the reported difference in the covalent radii of 1.22 for Co(III) and 1.40 for Rh(I).^J Although all other bond lengths are similar to those commonly found, the distance of 2.56 \AA between the two oxime oxygens appears to be consistent with a closed hydrogen bridge. It was felt that the data do not lend to the accurate determination of the hydrogen positions, and they were thus calculated.

As was found in the similar Co chelate^I, the metal atom is in the plane of the four nitrogen atoms as is indicated in Table IV. In addition the whole macrocycle is relatively planar with the exception of C_{10} in the three carbon bridge which is out by 0.70 \AA . As is also given in Table IV, there is a small angle between the two halves of the chelate, but this can perhaps be best described as a slight twist of the whole molecule.

Of final and perhaps most interest is the intermolecular arrangement of adjacent molecules. Although a stacked columnar arrangement might have been expected, such an ordering was not found. In the structure, the molecules are layered and staggered so that the $\text{C}_2\text{--C}_3$ bond of one molecule lies 3.5 \AA

above and below the C_6 -- C_7 bonds of its two nearest parallel neighbors.

This columnar stacking is replicated throughout the structure. It appears that this feature must account for the observed physical properties since, as is detailed in Table V, the nearest Rh-Rh distance is 6.7 Å.

Table IV: Molecular Planes^a

1. Plane Containing N(1), N(2), N(3), and N(4)

Unit Vector: $-0.5153X + 0.0090Y - 0.8570Z = -2.6436$

<u>Atoms</u>	<u>Distance from Plane, Å^o</u>
Rh	0.0074
O(1)	-0.0036
O(2)	-0.0200
C(2)	-0.0035
C(3)	0.0187
C(6)	0.0128
C(7)	0.0078
C(9)	-0.0461
C(10)	-0.6988
C(11)	0.0437

2. Plane Containing C(1), C(2), C(3), and C(4)

Unit Vector: $-0.5235X - 0.0278Y - 0.8516Z = -2.8092$

<u>Atoms</u>	<u>Distance from Plane, Å^o</u>
Rh	0.0360
N(1)	0.0462
N(2)	-0.0304

3. Plane Containing C(5), C(6), C(7), and C(8)

Unit Vector: $-0.4987X + 0.0038Y - 0.8667Z = -2.7491$

<u>Atoms</u>	<u>Distance from Plane, Å^o</u>
Rh	0.0474
N(3)	-0.0042
N(4)	0.0278

4. Angles Between Planes

<u>Planes</u>	<u>Angle, deg</u>
1 - 2	2.18
1 - 3	1.14
2 - 3	2.46

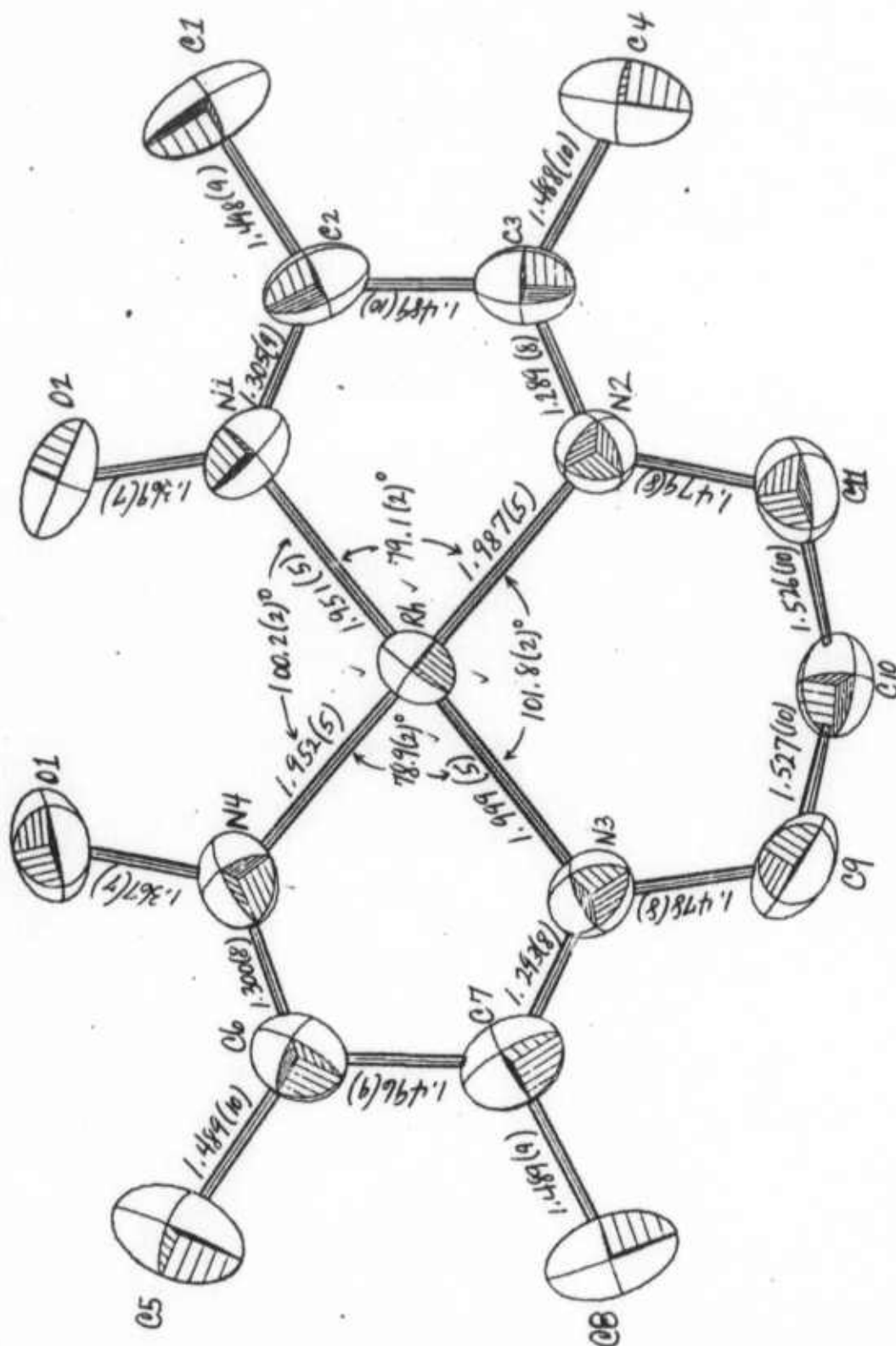
Table V. Selected Intermolecular Bond Distances (Å)
and Angles (DEG)

Rh(1)-Rh(4)	6.747(11)
Rh(1)-Rh(2)	10.095(11)
Rh(1)-Rh(3)	15.784(19)
Rh(4)-Rh(1)-Rh(2)	137.83(6)
Rh(4)-Rh(1)-Rh(3)	45.80(4)

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
2	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
3	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
4	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
5	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81																			



Transport in Iridium Carbonyl Halides

R. H. Bube and J. McKenzie

Approximately twelve samples of $\text{Ir}(\text{CO}_3)\text{Br}$ and twenty of $\text{Ir}(\text{CO}_3)\text{Cl}$ were formed by sublimation on glass substrates in an attempt to determine the dependence of the sample structure on three parameters: substrate temperature, source or chamber temperature, and CO pressure. Heat-sink compound was used to attach the substrate to the end of a cold finger. Previously prepared $\text{Ir}(\text{CO}_3)\text{Cl}$ or $\text{Ir}(\text{CO}_3)\text{Br}$ was dried under vacuum at 100-120°C, the chamber was pressurized with CO and the temperature raised to the operating level (135-155°C), and the cold finger was chilled. After the substrate appeared to have the desired amount of material (typically about 0.5 mg/cm²), the heater was turned off and the chamber evacuated. The same process with a high CO pressure (greater than 500 Torr) was used to produce $\text{Ir}(\text{CO}_3)\text{Cl}$ from IrCl_3 .

For both of the two compounds, the sample structure ranged from a heavy mat of intertwined needle-shaped crystals to a film whose structure was not resolvable with a 120X microscope. The conditions favoring production of large needles were a relatively warm substrate greater than 80°C, and a chamber temperature of about 135-140°C with no discernible dependence on CO pressure in the range of 25-750 Torr. Preheating the $\text{Ir}(\text{CO}_3)\text{Cl}$ with CO at greater than 750 Torr seemed to increase the yield. The finest grain was favored by significantly colder substrates - dry ice and acetone cooled to about 200°K, or liquid nitrogen cooled to 77°K, and lower CO pressures (much less than 25 Torr) for consistency.

The growth of the samples seems to proceed in stages. First, a smooth or extremely fine grain layer appeared, then nucleation followed by radial growth of needles which would eventually interweave to form a mat. The nature of this meshing, in particular the orientation, strongly affected the appearance, including the color. Many films were not very homogeneous; some had the full range of possibilities from bits of Ir, fine grain, needles, and even patches of what appeared to be IrCl_3 or IrBr_3 . The needles of $\text{Ir}(\text{CO}_3)\text{Br}$ in both the

material produced by Joan Valentine and in our samples, as well as the fine grained layers, possessed a metallic luster not unlike that of Ir. These appeared darker immediately after heating with CO and if exposed to the atmosphere gradually lightened in appearance over a period ranging from days to weeks. The smooth or fine-grained films of $\text{Ir}(\text{CO}_3)\text{Cl}$ were yellow in color, while the needles were darker. Neither appeared to change with time.

Preliminary measurements were performed on some of these samples. Both a sublimed film of $\text{Ir}(\text{CO}_3)\text{Br}$ and a cluster of $\text{Ir}(\text{CO}_3)\text{Br}$ needles had an activation energy for electrical conductivity of 0.21 eV, and a thermoelectric power between 450 and 520 $\mu\text{V}/^\circ\text{K}$ for temperatures between 225 and 330 $^\circ\text{K}$. For a film of $\text{Ir}(\text{CO}_3)\text{Cl}$ and a bundle of crystalline strands, the activation energy for electrical conductivity was approximately 0.17 eV, while the thermoelectric power for the strands lay between 450 and 520 $\mu\text{V}/^\circ\text{K}$, and that for the $\text{Ir}(\text{CO}_3)\text{Cl}$ film was of the same order of magnitude. These values of thermoelectric power would correspond in a "semiconductor" interpretation to a hole density of the order of $2 \text{ to } 4 \times 10^{16} \text{ cm}^{-3}$. The relative temperature independence of the thermoelectric power indicates a thermally activated hole mobility.

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